Probing Chemical Bonding Using X-ray Spectroscopy

Anders Nilsson
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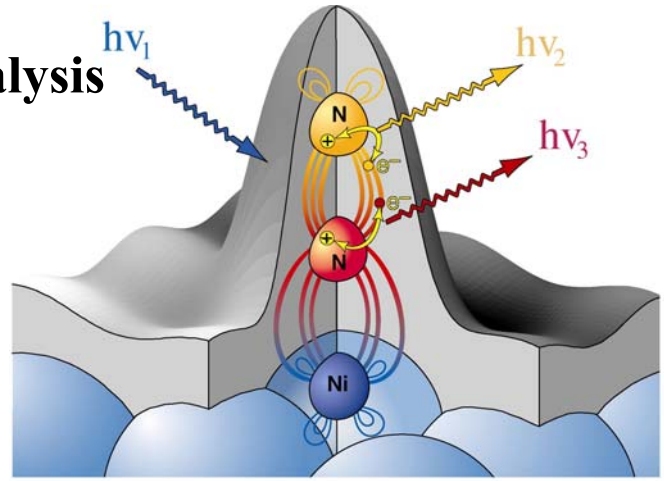
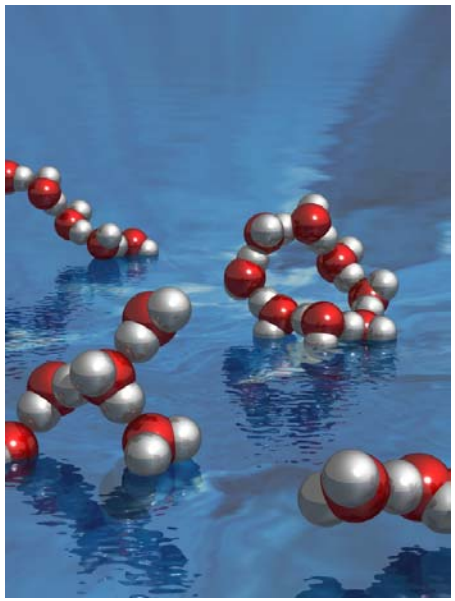
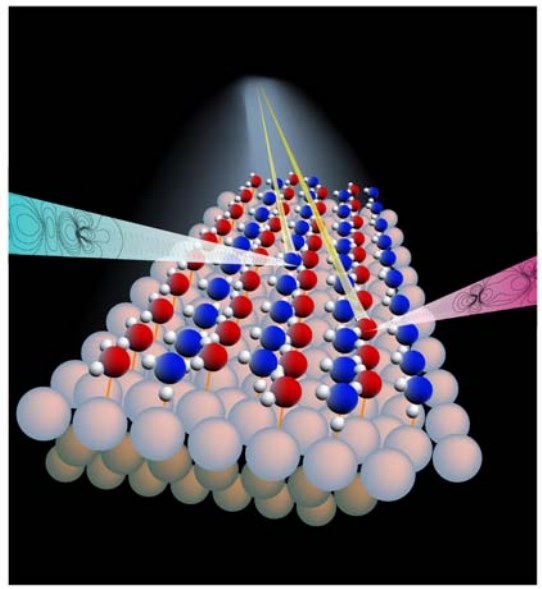
Chemical Bonding in Catalysis





The structure of liquid water



Bonding of adsorbed water

Coworkers

Lars Pettersson/SU

Mats Nyberg/SU

Luciano Triguero/SU

Hirohito Ogasawara/Stanford and SU

Dennis Nordlund/SU

Barbara Brena/SU

Henrik Öström/SU

Klas Andersson/Stanford and SU

Lars Åke Näslund/Stanford and SU

Theanne Schiros/Stanford and SU

Michael Odelius/SU

Philippe Wernet/Stanford

Uwe Bergmann/Stanford

Alexander Föhlich/UU

Jörgen Hasselström /UU

Nial Wassdahl /UU

Olof Karis /UU

Peter Bennich /UU

Tomas Wiell /UU

Martin Weinelt /UU

Jens Norskov/DTU

Bjorg Hammer/UÅ

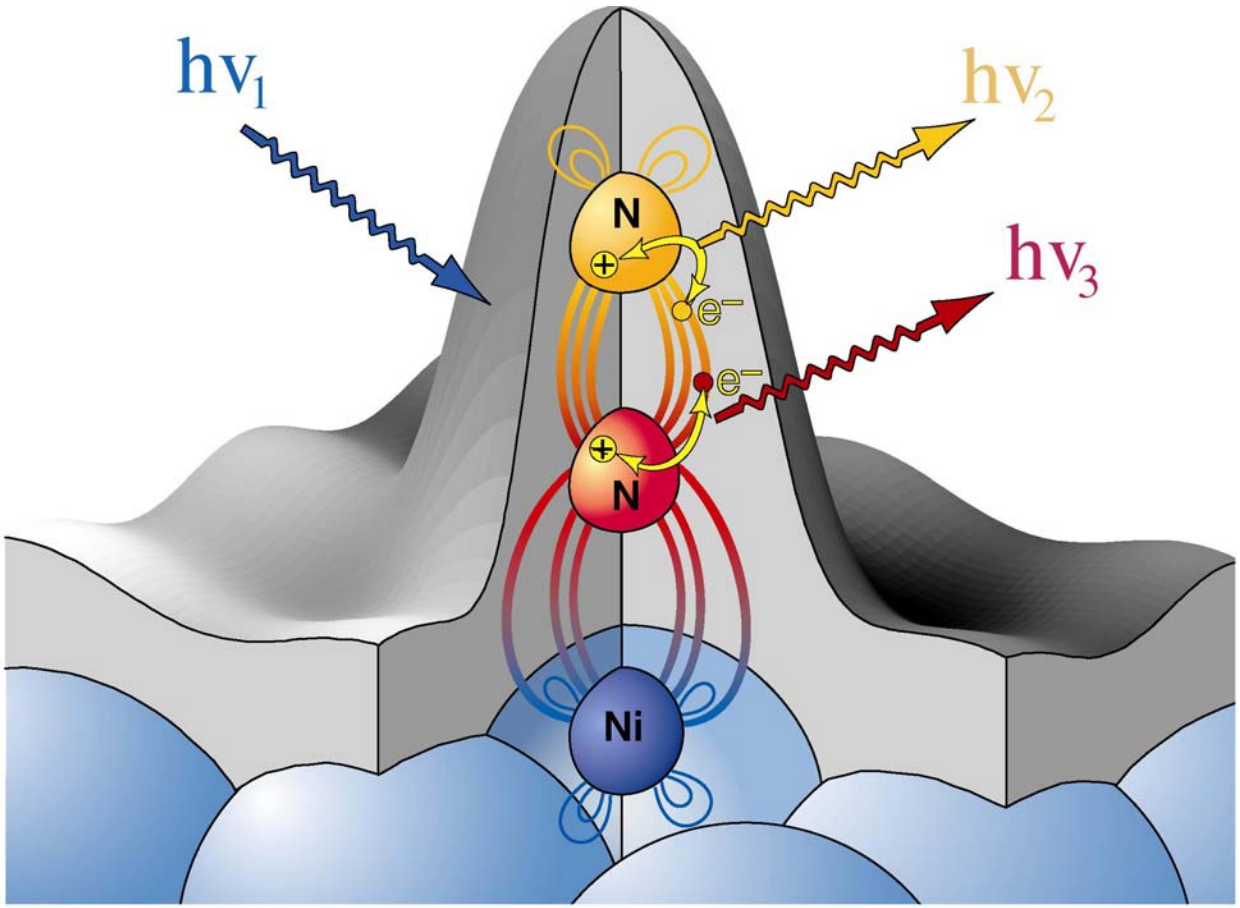
Clemens Heske/WU

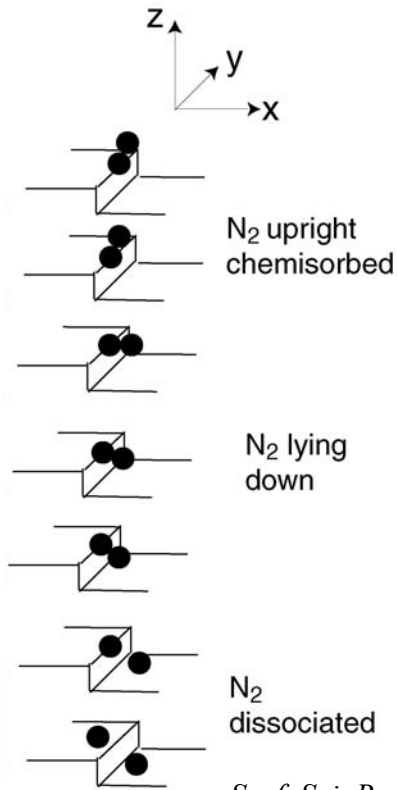
Satish Myneni/Princeton

Chemical Bonding and Catalysis

Haber-Bosch

$$N_2 + 3H_2 \rightarrow 2NH_3$$



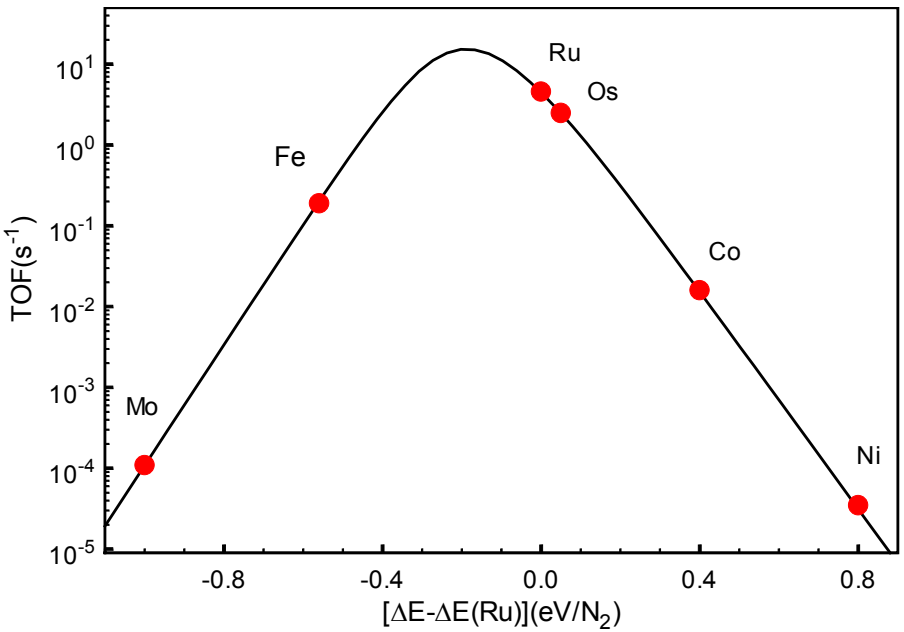


Surf. Sci. Reps. **55** (2004) 49.

Ammonia synthesis

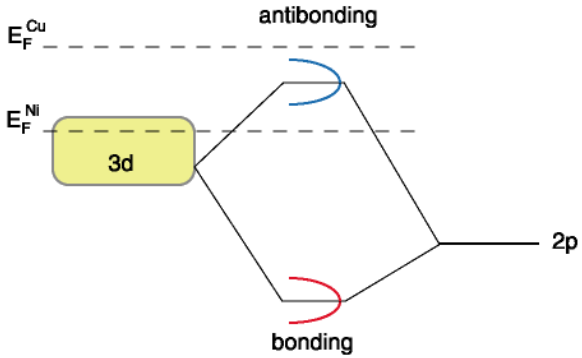
Haber-Bosch

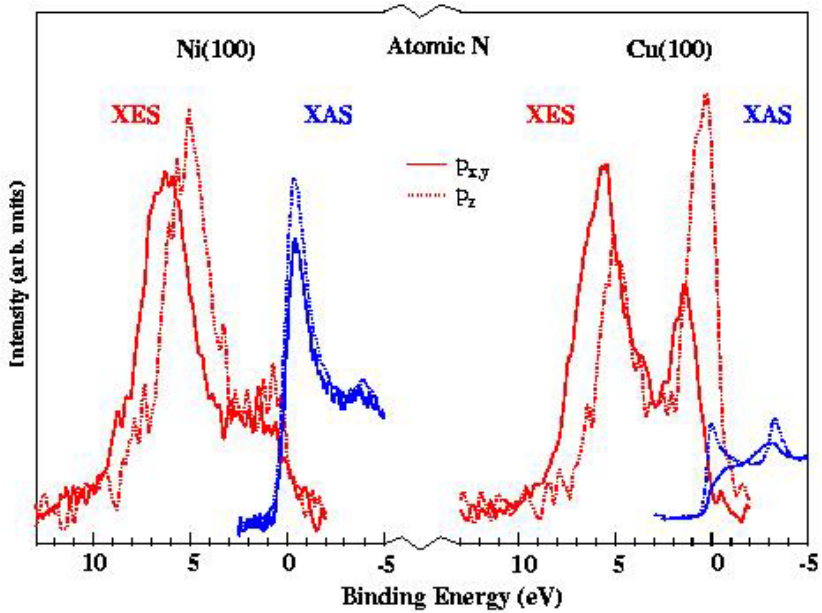
$$N_2 + 3H_2 \rightarrow 2NH_3$$

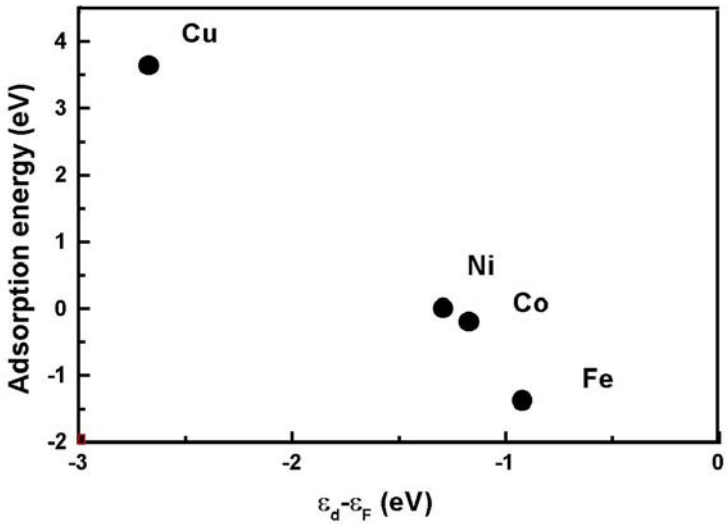


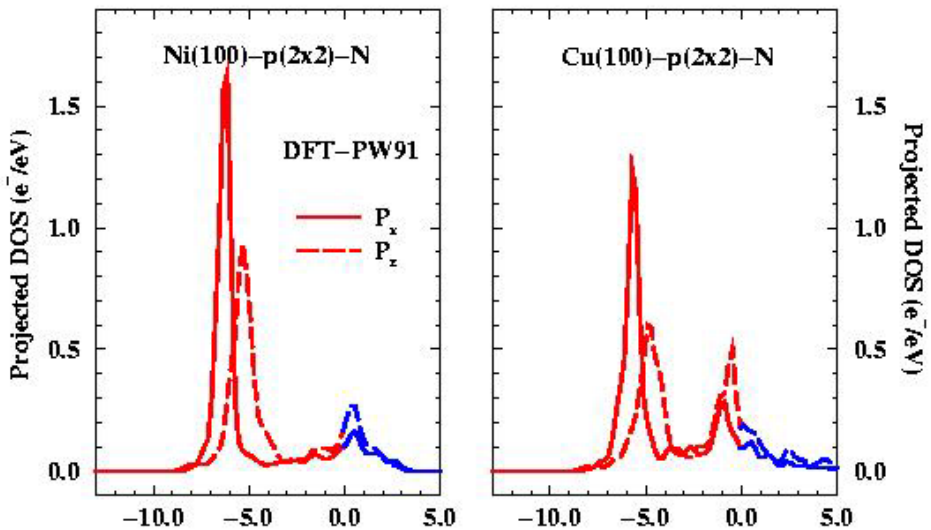
Reaction rate versus N-metal adsorption energy

Electronic Effect in Catalysis





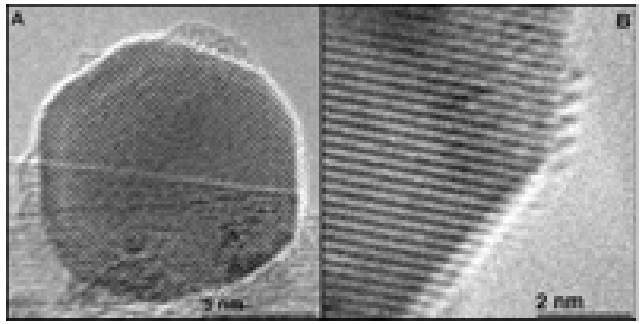




Femtosecond Chemistry

Haber-Bosch

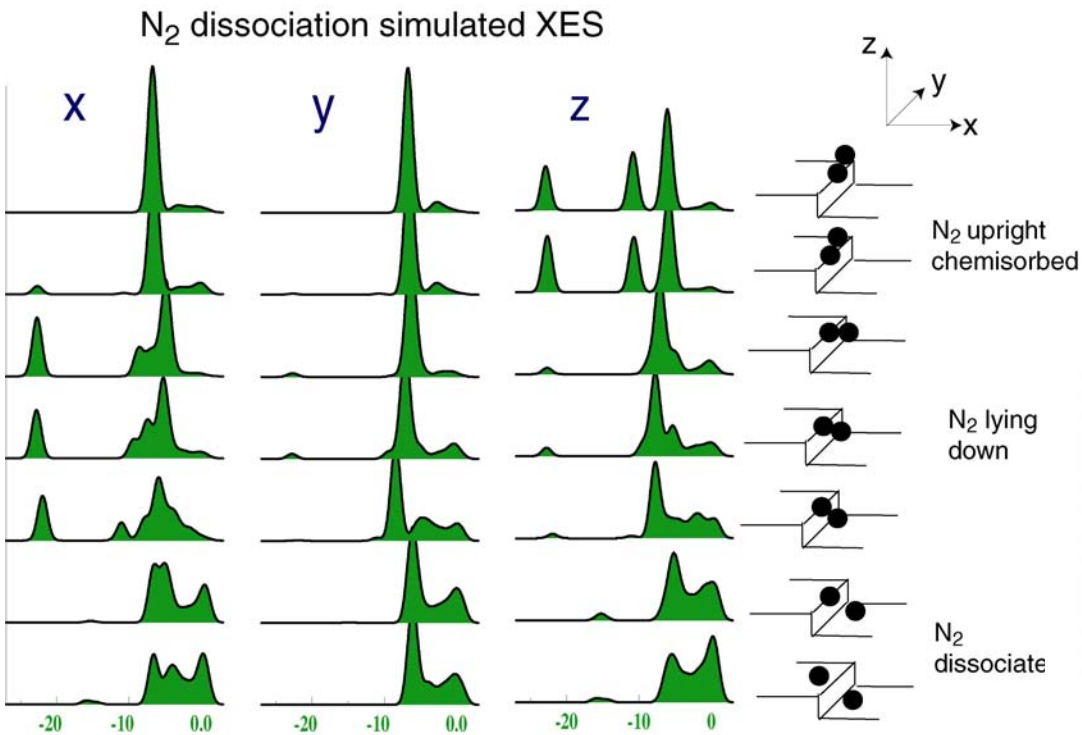
$N_2 + 3H_2 \quad 2NH_3$



Hansen et.al. Science 294, 1508 (2001)

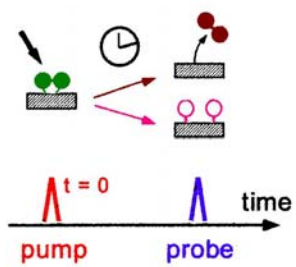
New Ru Catalyst

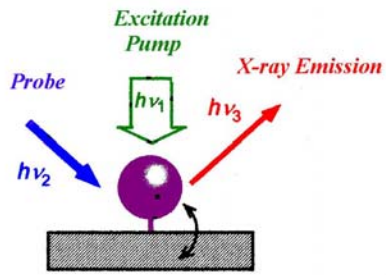
Active site at steps



Both N atoms

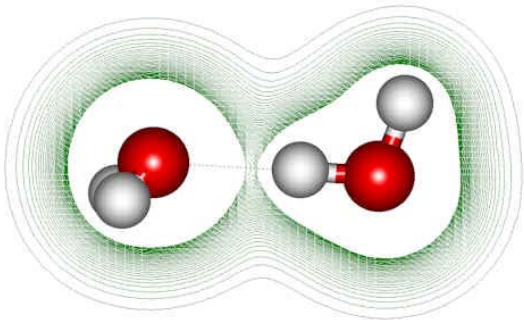
Theoretical simulations, Mats Nyberg, Stockholm University





Probe pulse at different delay time Δt

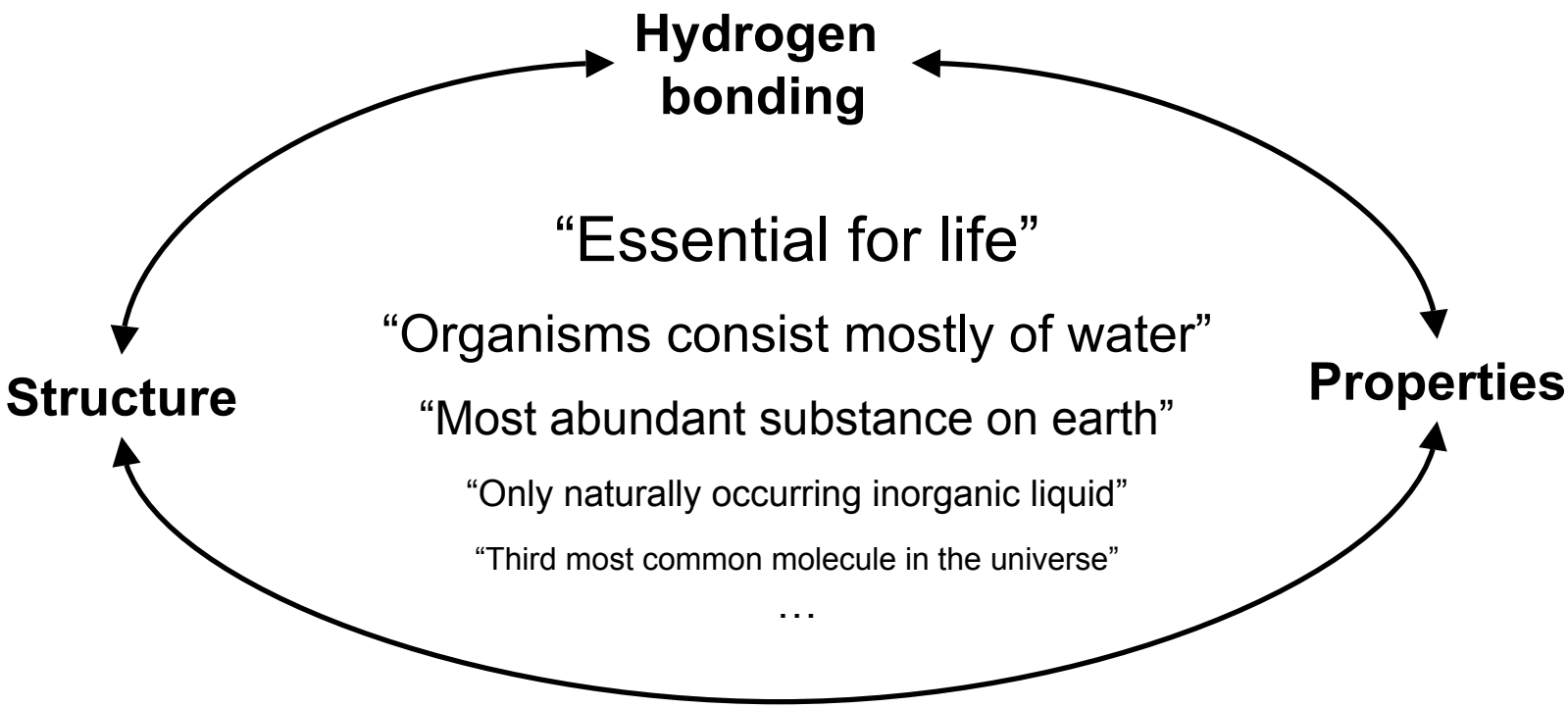
Hydrogen Bonding and Water



H-bonds are formed between H and N, O and F atoms

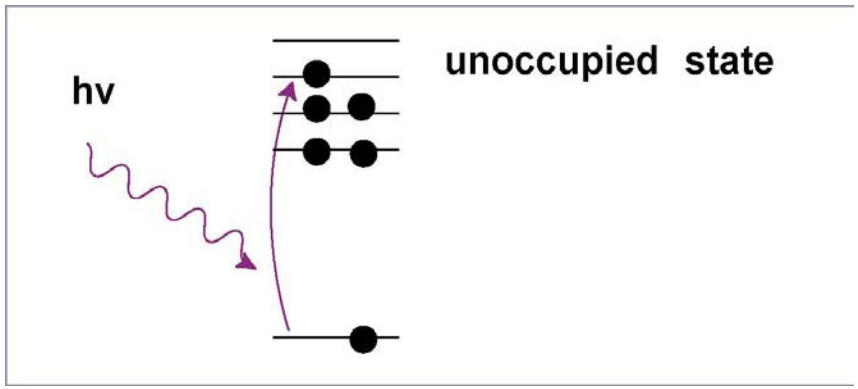
They are weak and easily broken and reformed

The valence electrons are strongly affected by H-bonds and can be probed using X-ray spectroscopy

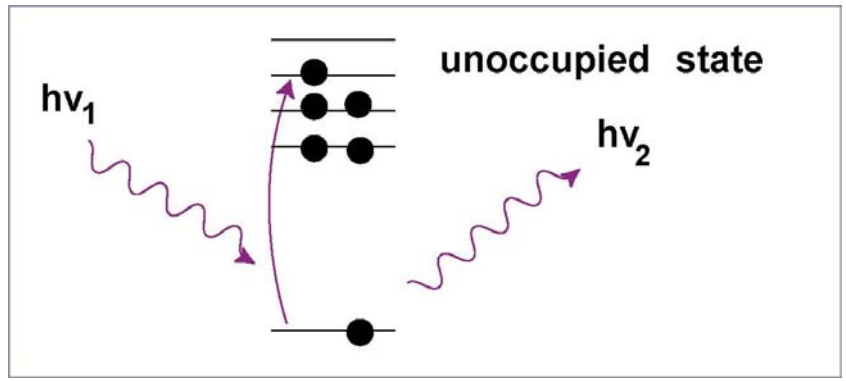


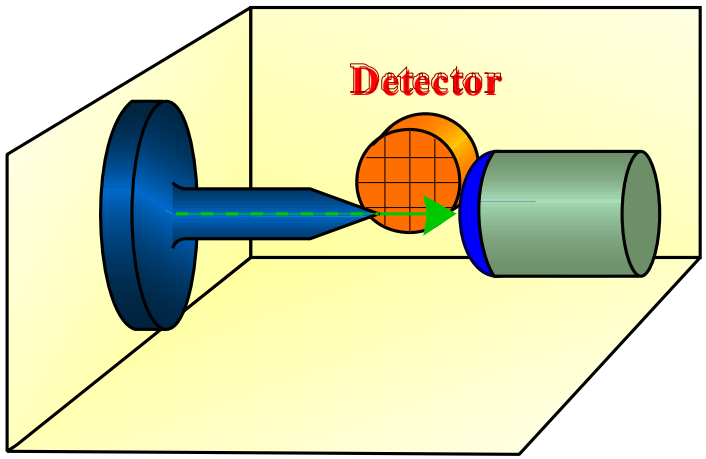
X-ray Absorption Spectroscopy

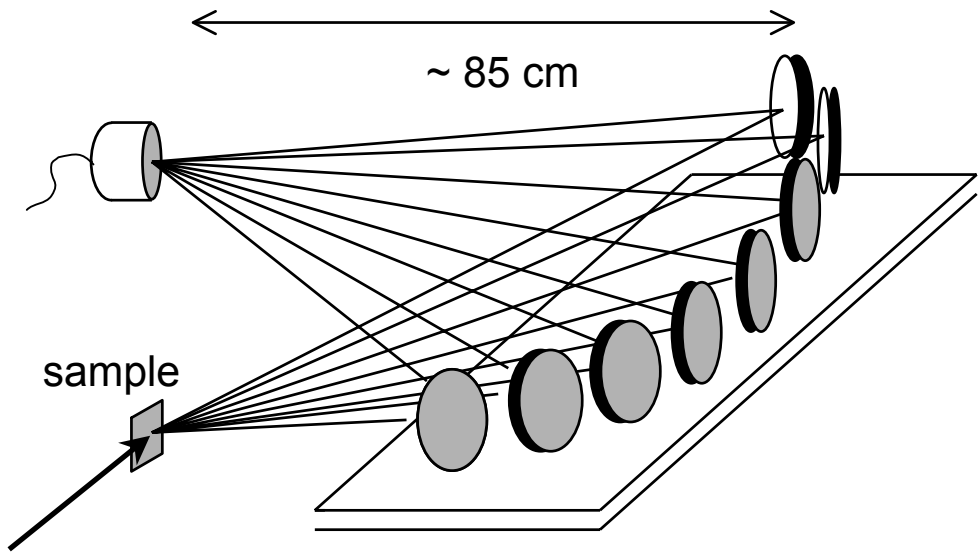
Soft X-rays Absorption



X-ray Raman spectroscopy

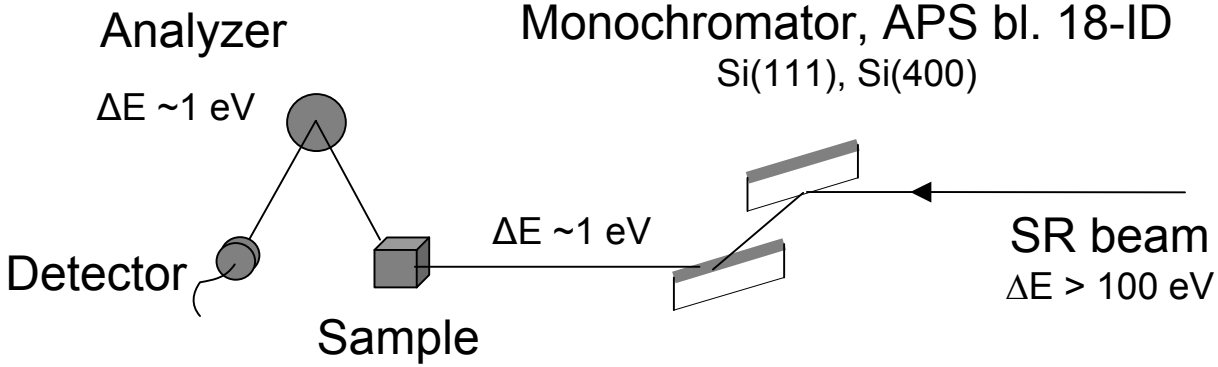


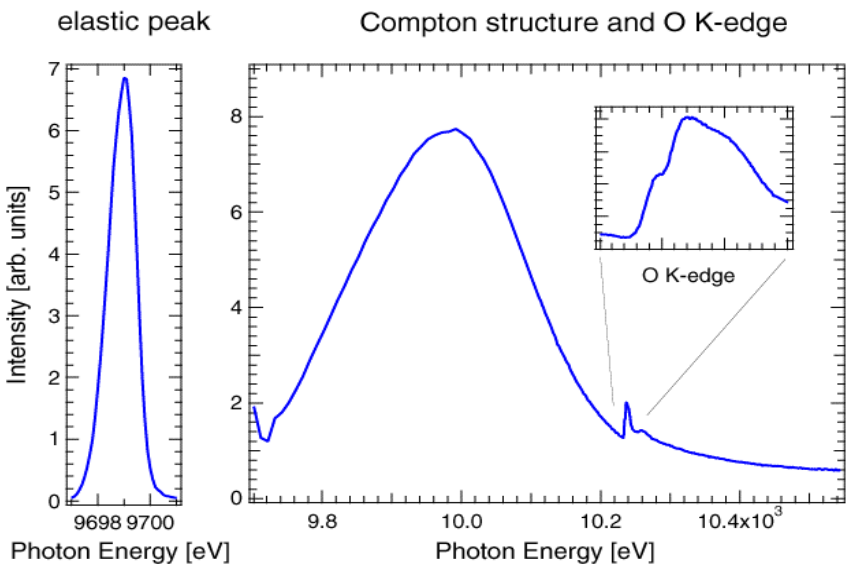




Water Raman Scattering Set-up

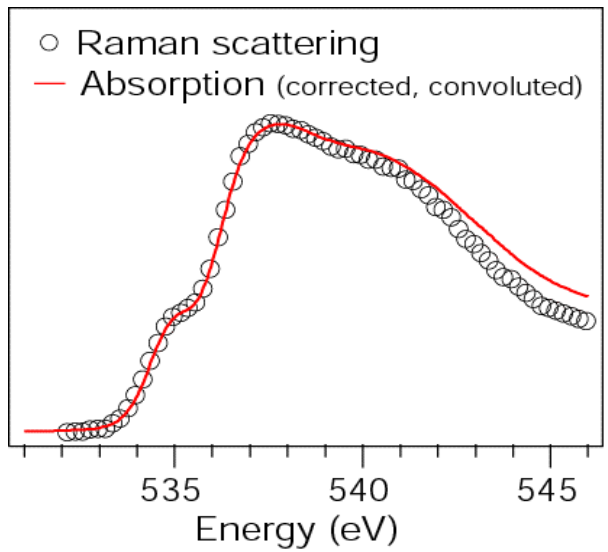
Bergmann and Cramer, SPIE Proceedings **3448**, 198 (1998)





Bergmann, Wernet, Glatzel et al., PRB **66**, 092107 (2002).

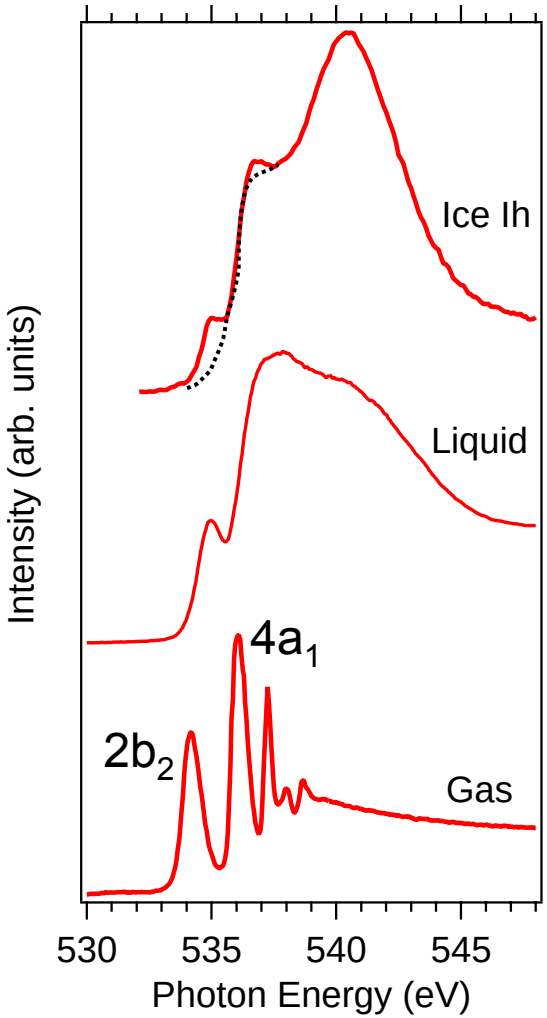
Si(440), 88°, 6.46 keV, q=4.2 Å^{-1}

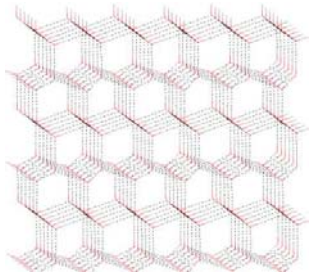


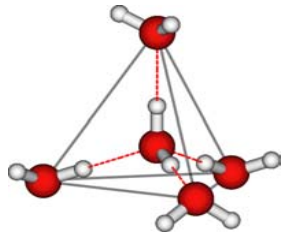
Correct for **saturation**

Probing depth **1 mm ↔ 1Å**

X-ray Absorption Spectroscopy of Water



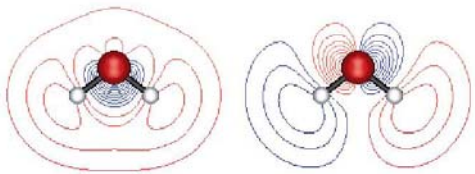




"…making and breaking of H-bonds…"

⇩

?



$4a_1$ $2b_2$

Hydrogen bonding

Conduction band formation
Local symmetry

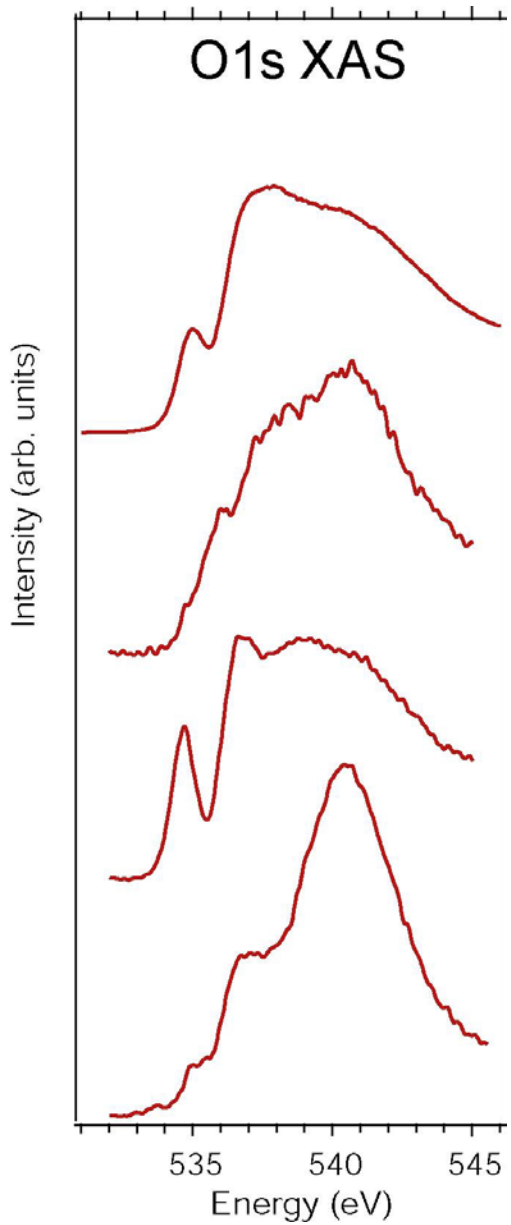
⇩

O K-edge XAS:

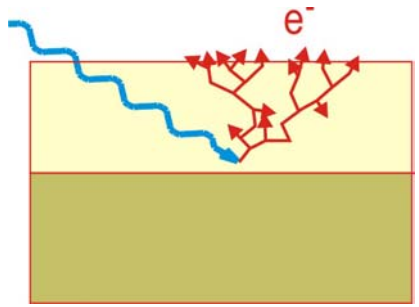
ultra-fast, element-specific, symmetry-sensitive and local probe for the structure of water.

Myneni et.al. J. Phys. Condens. Matter 14 (2002) 213

Comparison with ice surface

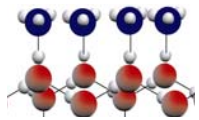


Soft X-rays



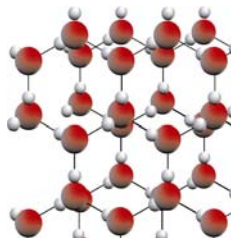
water

ammonia terminated ice surface

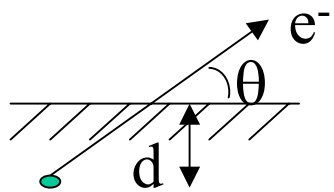


Auger Yield

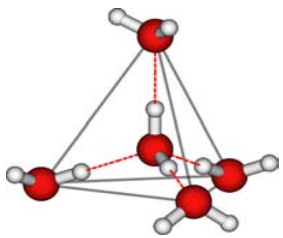
surface of ice



$$I = I_0 \exp(-d/\lambda \sin\theta)$$



bulk ice



Wernet et. al. Science in press

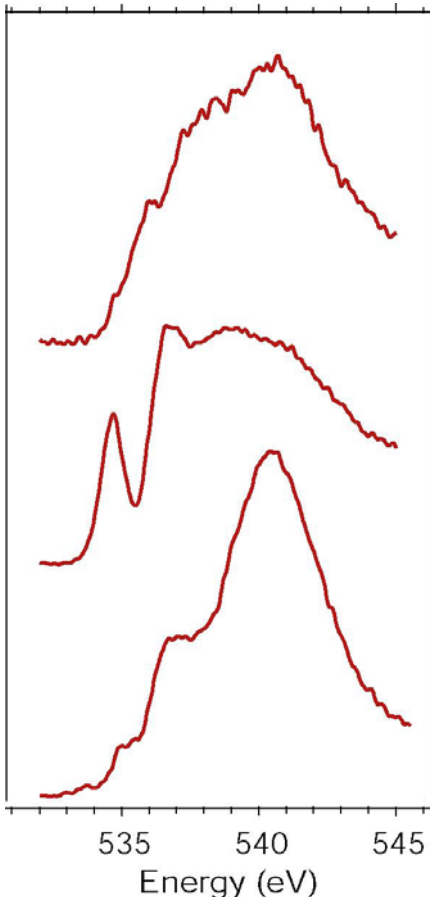
XAS spectral calculations

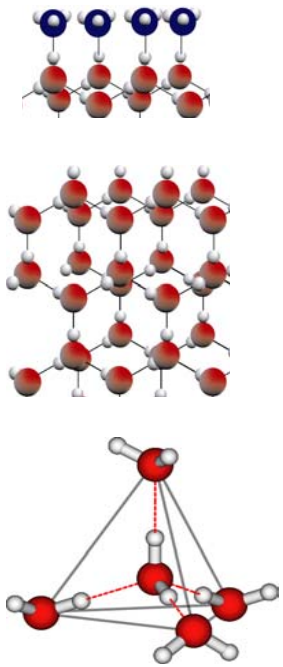
- Density Functional Theory (DFT)
- Transition potential calculation

Clusters of 24-44 molecules

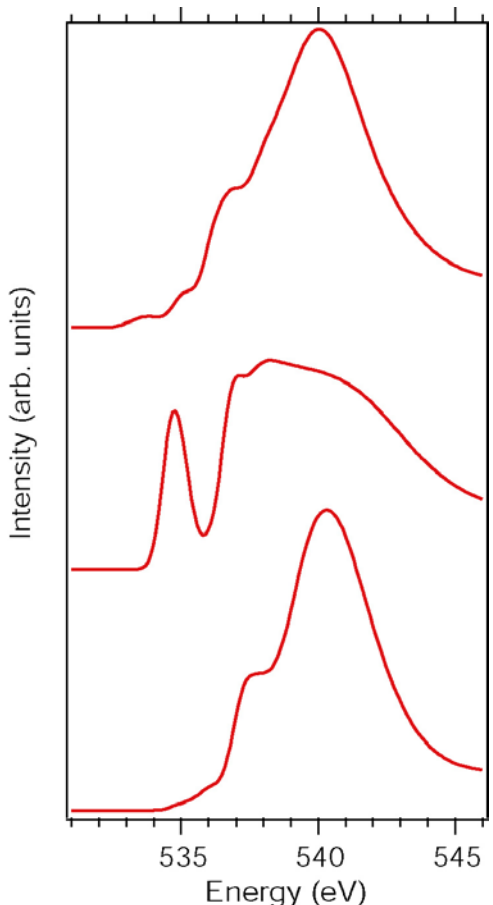
Model systems of ice

Experiment





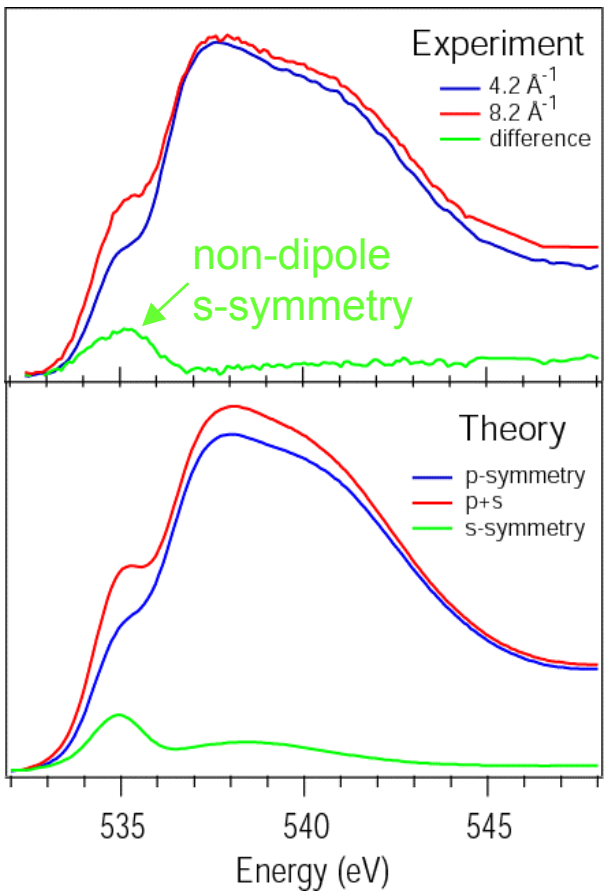
Theory

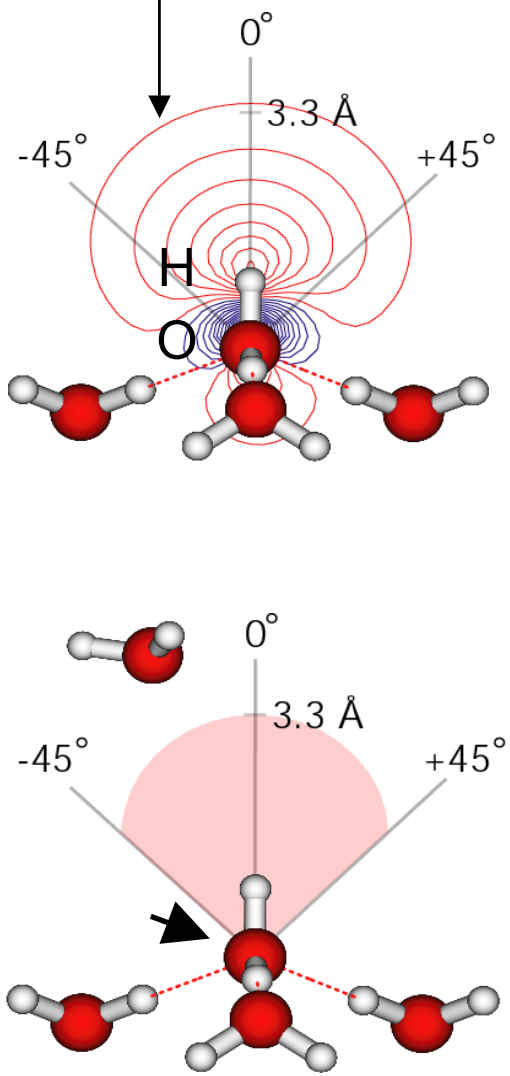


Symmetry: Probing s and p States

Pre-edge orbital:

Localized along O-H bond
Large s-contribution

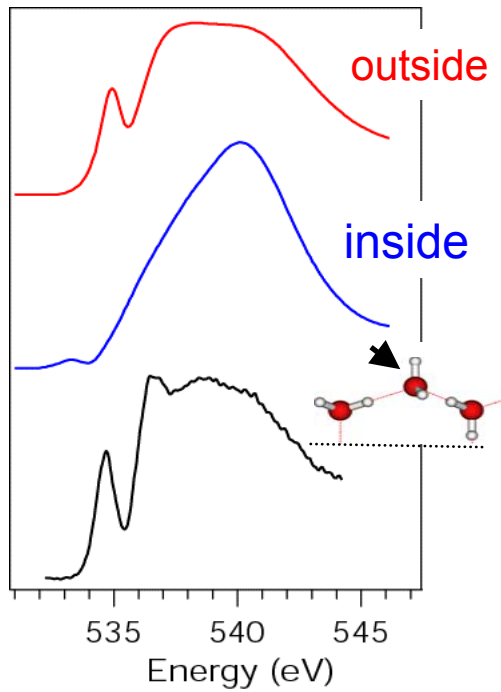




New H-bond definition
molecule
inside/**outside**
red area

⇩

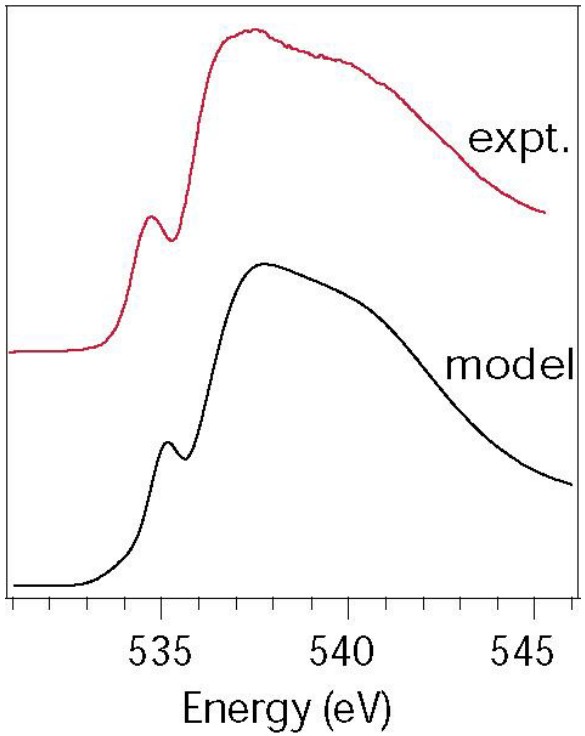
intact/**broken**



Bergmann et al., to be published (2004).

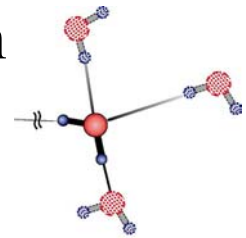
Wernet et al., Science **304**, 995 (2004)

Nearly all waters are SD species



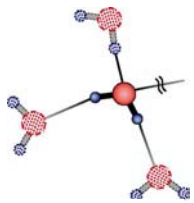
10% double donor
85% single donor
5% non donor

Comparing water spectrum with one theoretical spectrum

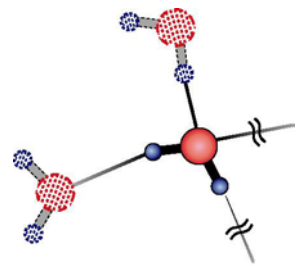


All waters Single Donor (SD) species?

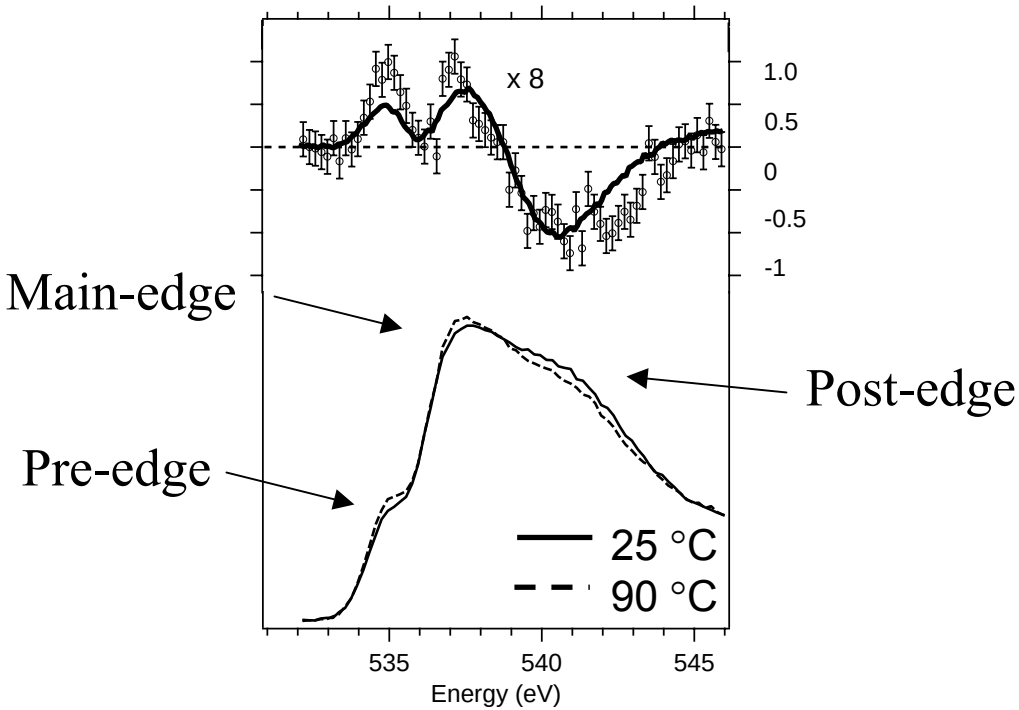
Symmetry requires the same amount broken H-bonds on oxygen side

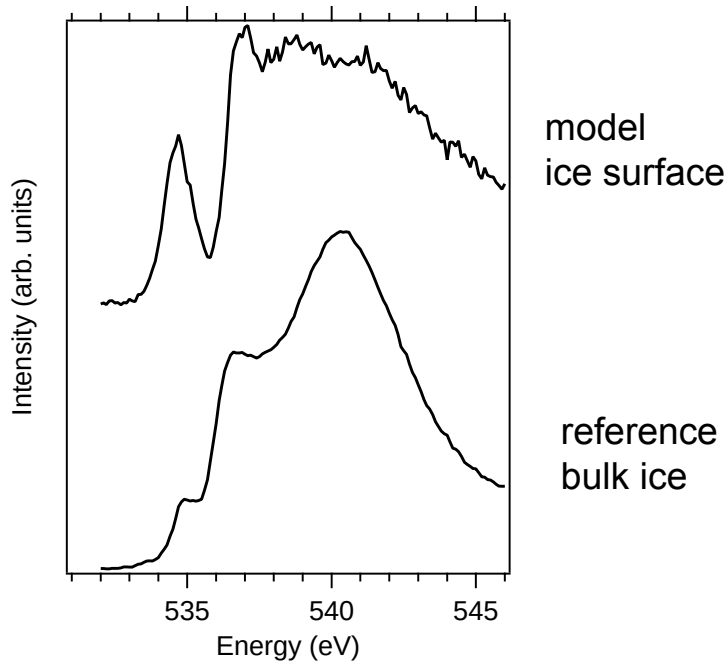


Most water molecules in 2 hydrogen bonded structures with broken donor and acceptor on both molecule



Temperature effects: Hot water



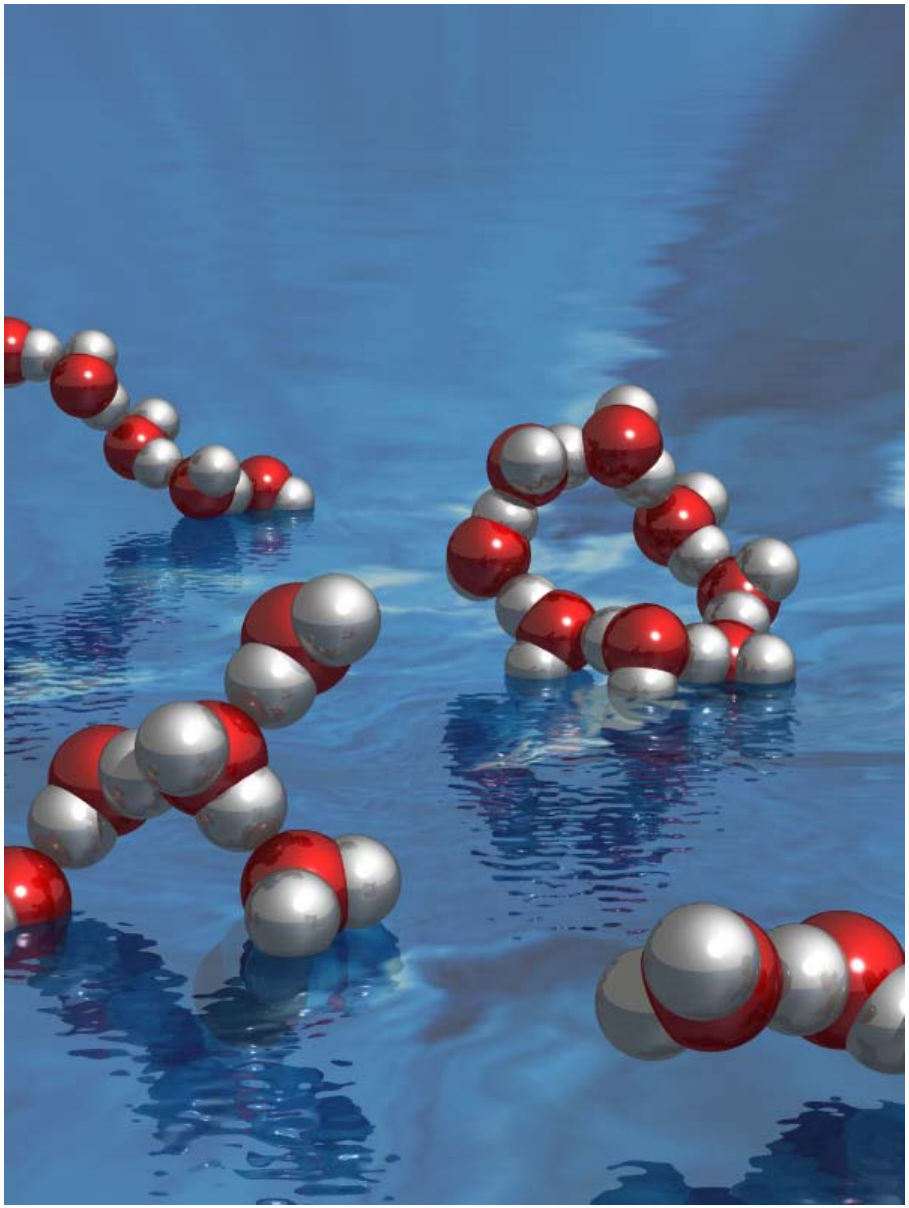


compare ambient water – bulk ice and 8 x (hot water – ambient water)

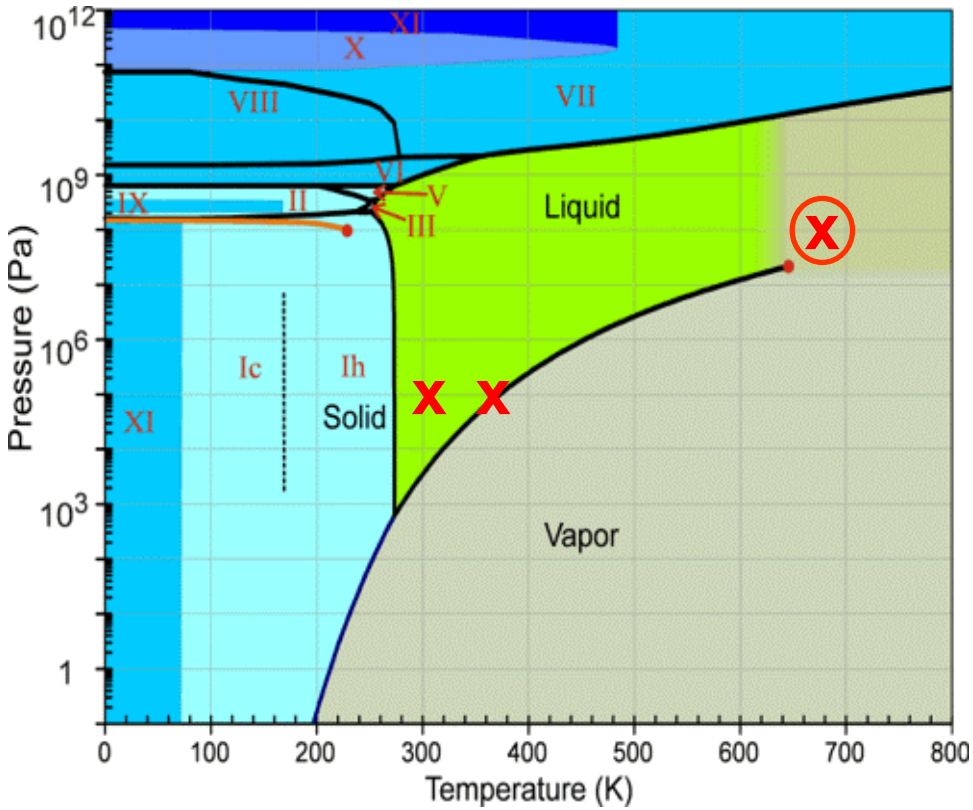
- ambient and hot water structure very similar
- changes in H-bond network upon heating and in phase transition very similar
- increase of free O-H, decrease of tetrahedral configurations
- approximately: two-component structure for water (isosbestic point)

Wernet et. al. *Science* **304**, 995 (2004)

The local structure of liquid water



Supercritical water



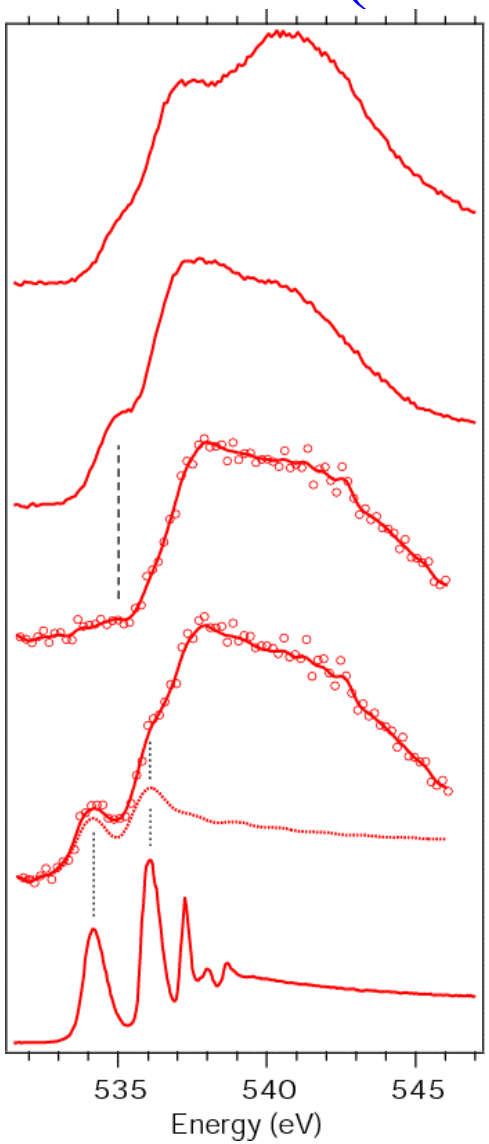
XRS

380 °C
300 bar
0.5 g/cm^3

- New phase
- Structure and bonding
- Properties of sc water
- Solvent for organics
- …

XAS Supercritical Water

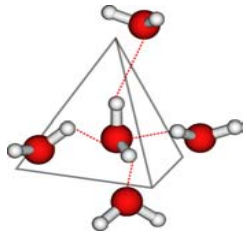
(300 bar, 380 °C, 0.54 g/cm^3)



Ice

Liquid water

Distorted tetrahedra



Difference
SC water – 35% vapor

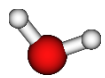
65% (±15%) H-bonded

SC water

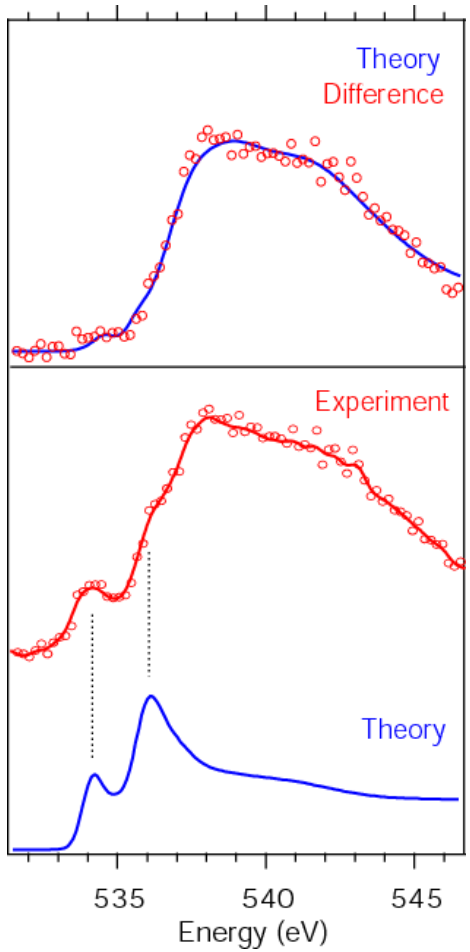
35% water vapor (convoluted)

35% (±15%) unbonded

Water vapor (absorption)

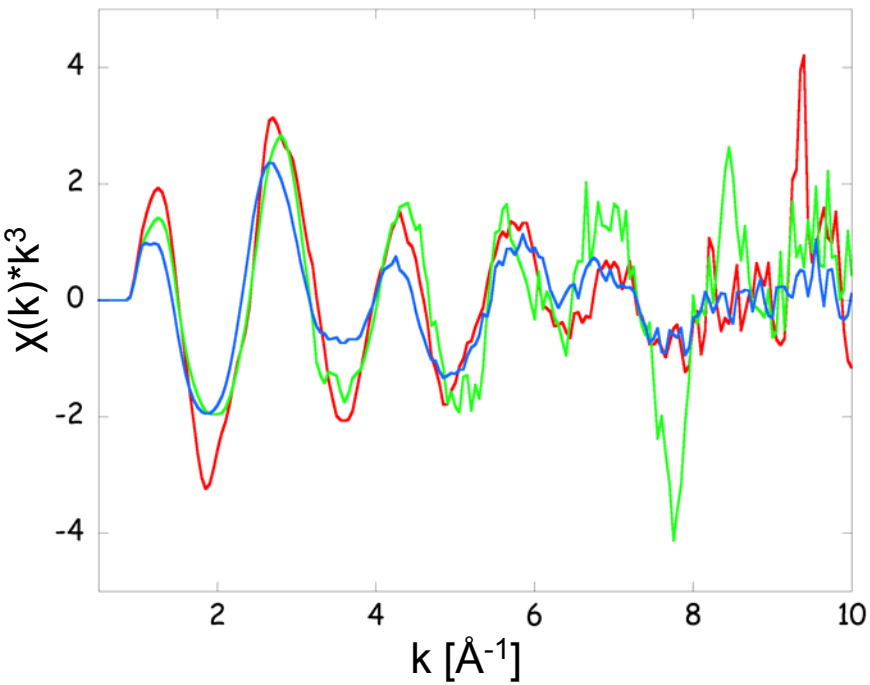


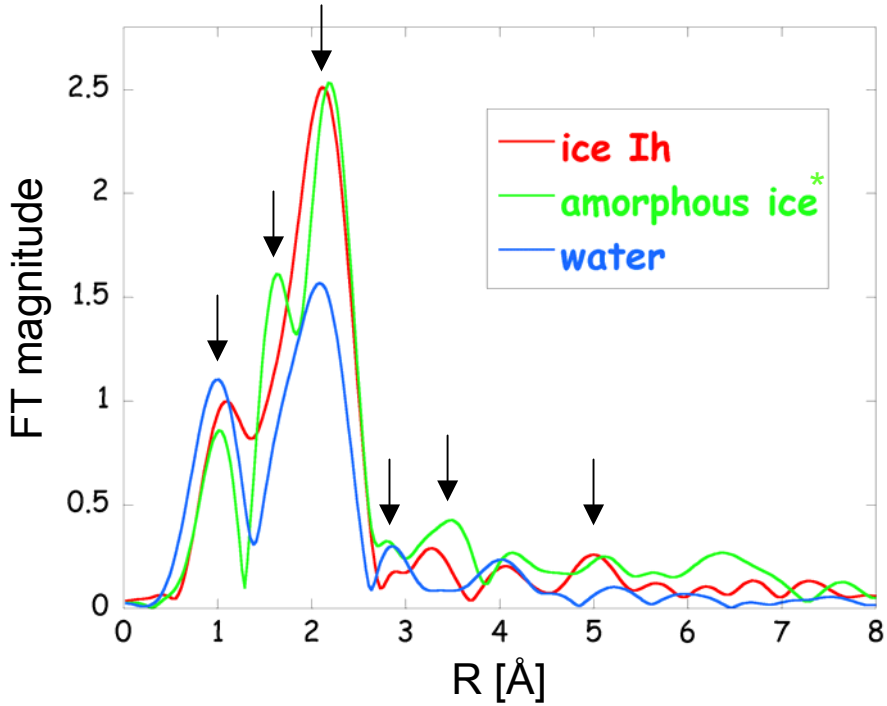
Gas-phase like



Wernet et al., submitted (2004).

EXAFS





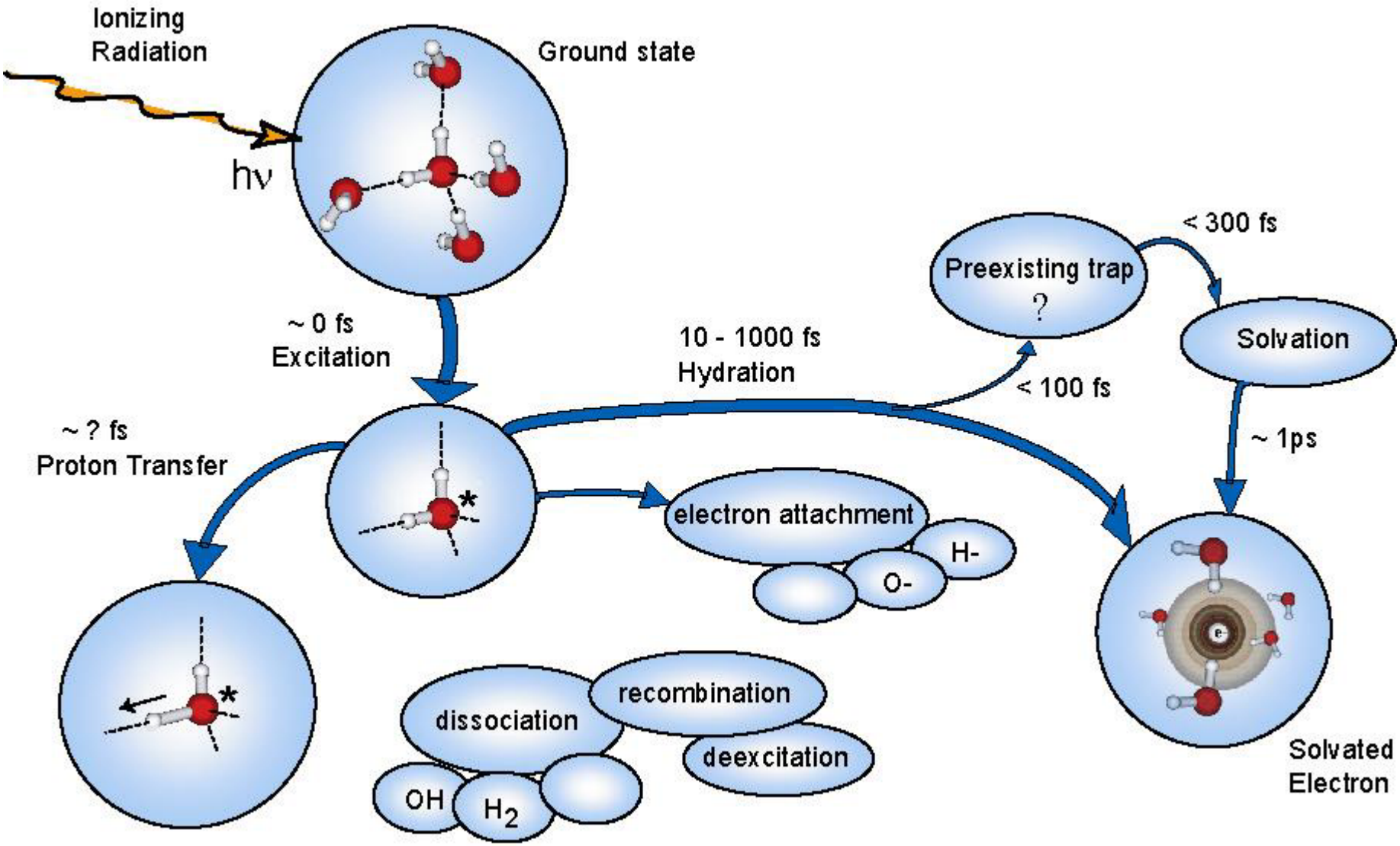
Bergmann et al., to be published (2004).

Data suggest (preliminary):

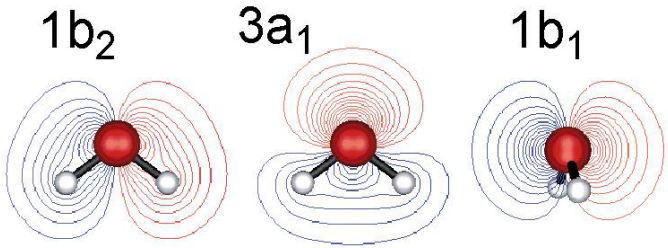
- Intra molecular O-H peak clearly observed
- Less intensity in water around 1.8 Å
- O-O distance similar in ice Ih and water, slightly larger in amorphous ice
- New peak in water at 2.9 Å as compared to ice Ih
- Peaks at ~3.5 Å and 5 Å absent in water

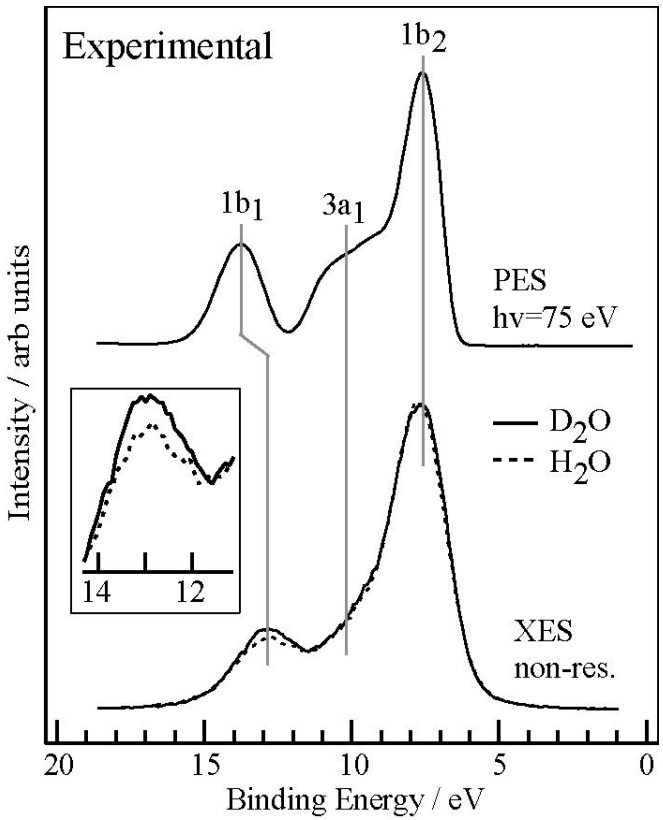
*Amorphous ice data taken in Auger electron yield from Zubavichus et al., ChemPhysChem **5**, 509 (2004).

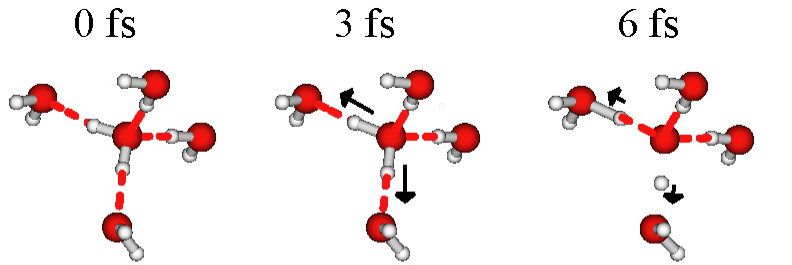
Ultrafast processes in ice

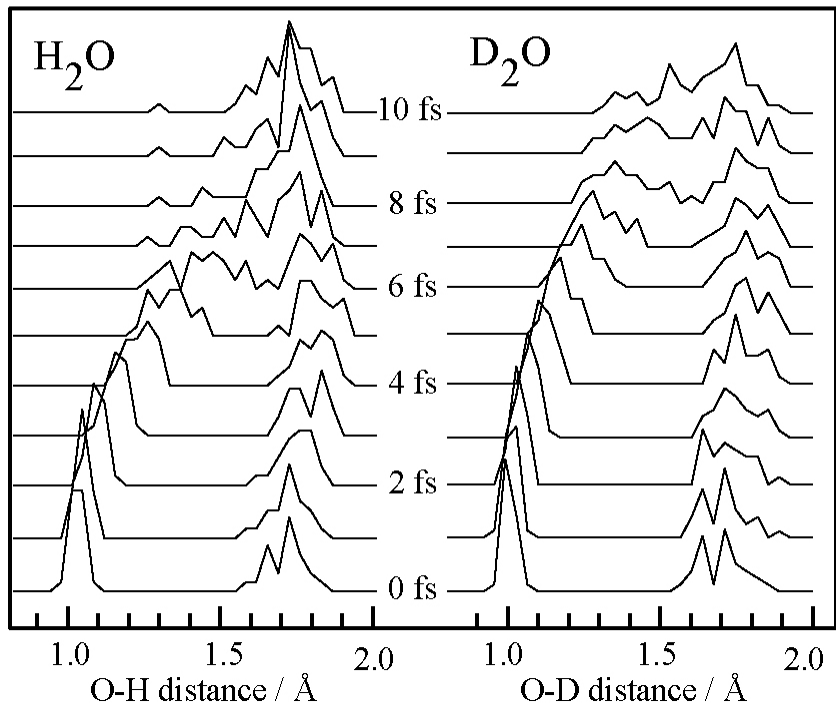


Water dissociation



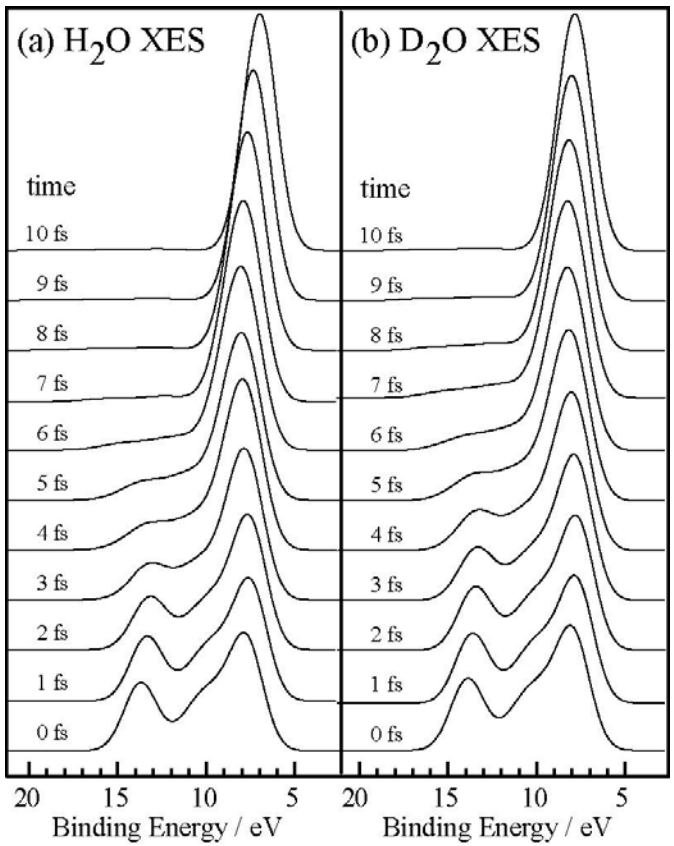


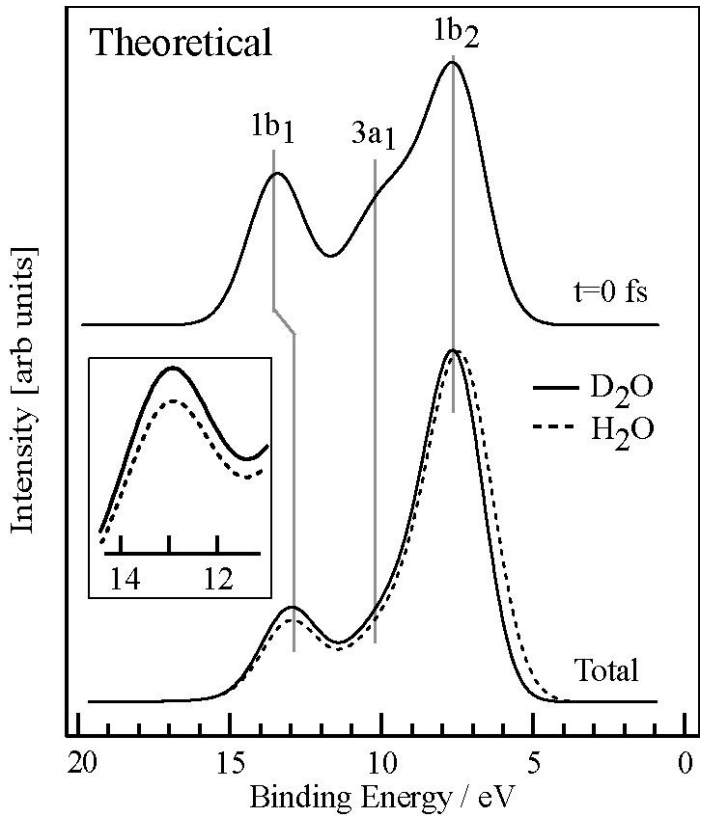




Phys. Rev. Lett. **93**, 148302 (2004).

Experimental spectra





O1s lifetime 3.6fs

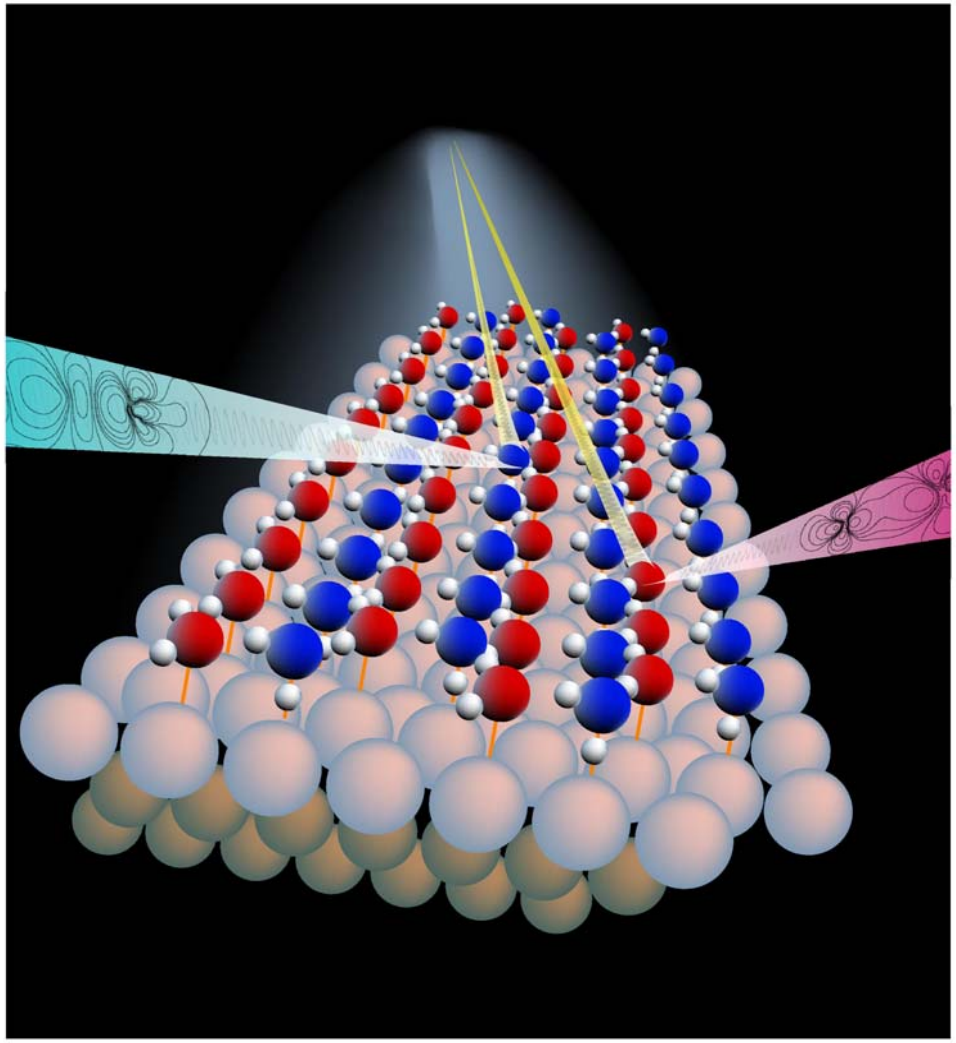
Water on metal surfaces

Electrochemistry

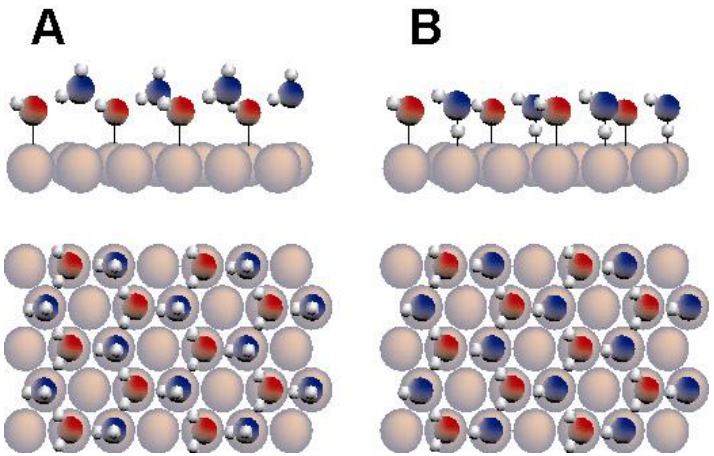
Corrosion

Fuel cell catalysis

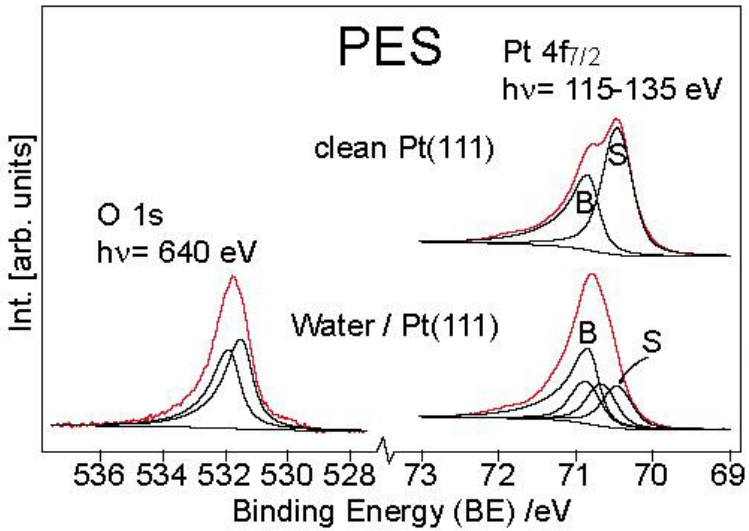
Hydrogen production

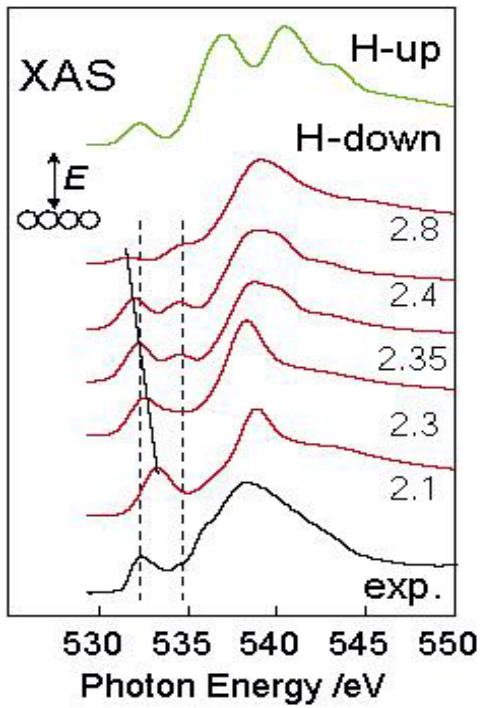


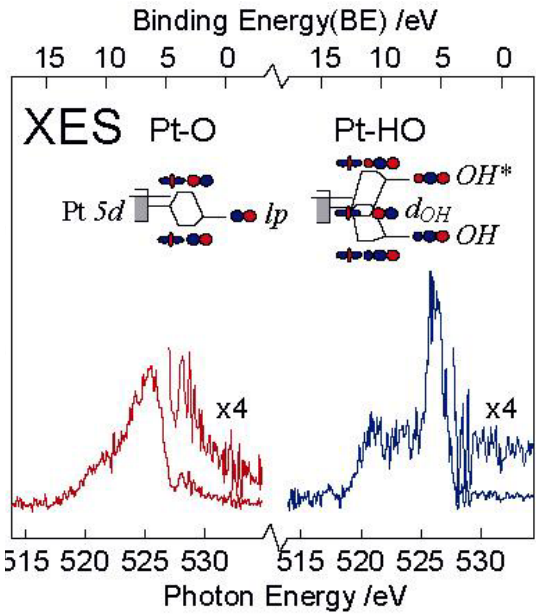
Water Adsorption on Pt(111)

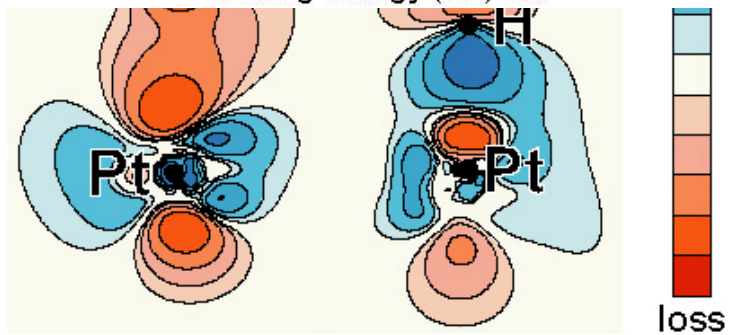


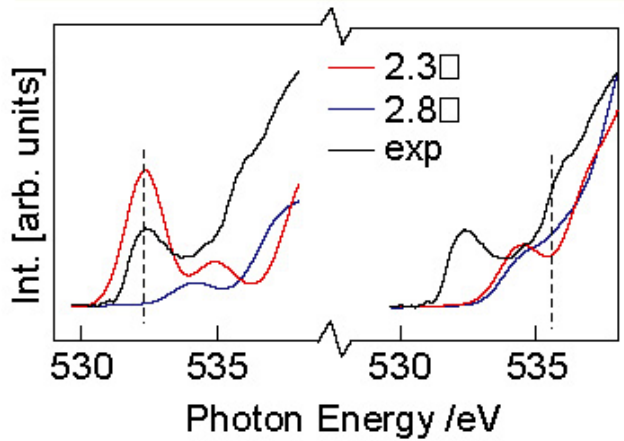
Old Bilayer model **New model**





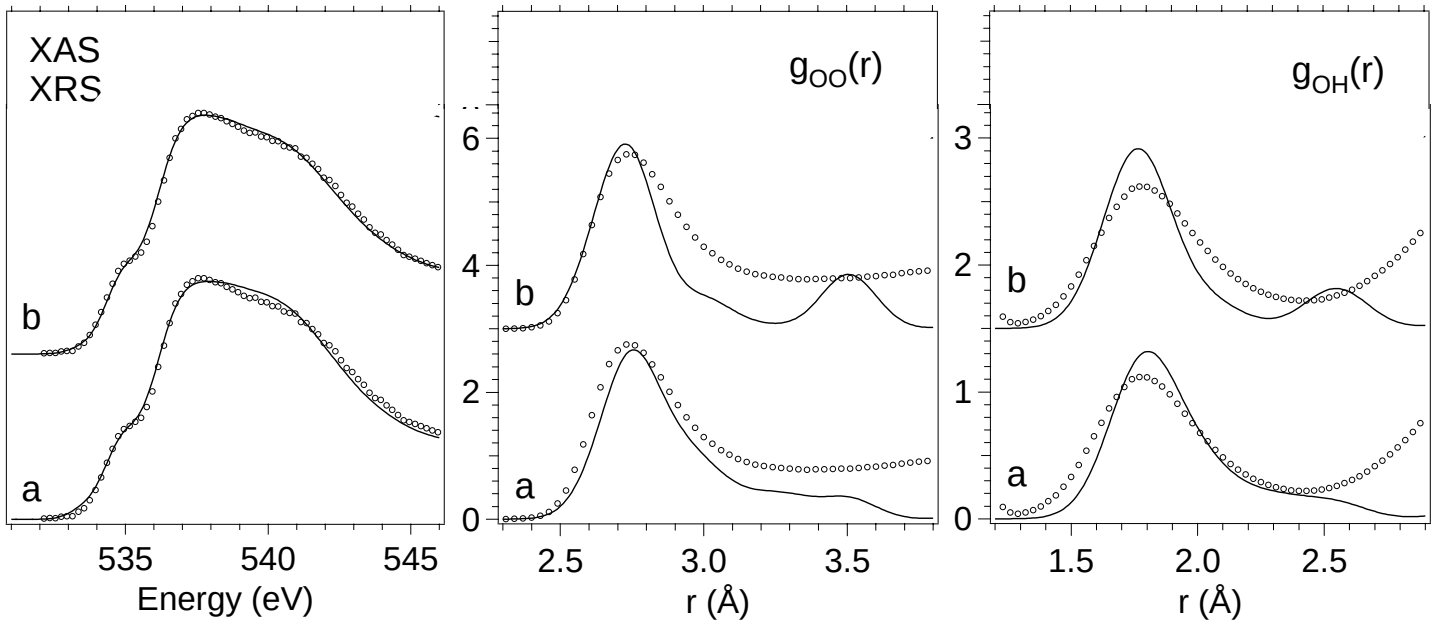






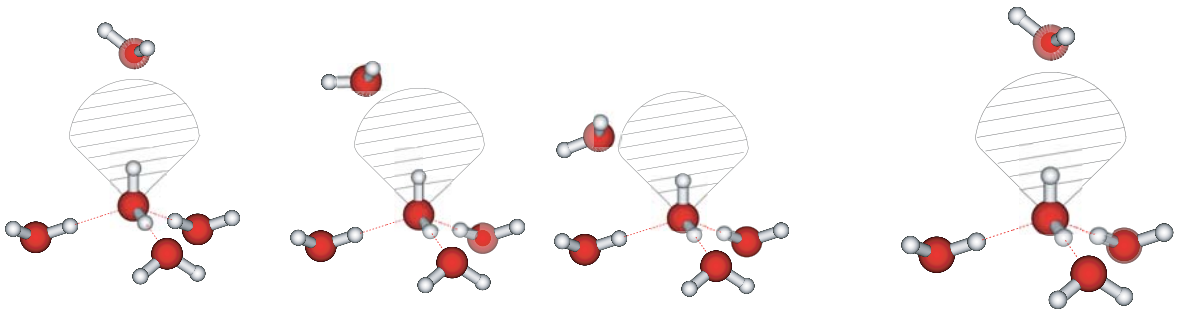
Ogasawara et. al. Phys. Rev. Lett. 89, 276102 (2002)

2 cases: broken H-bonds due to bending

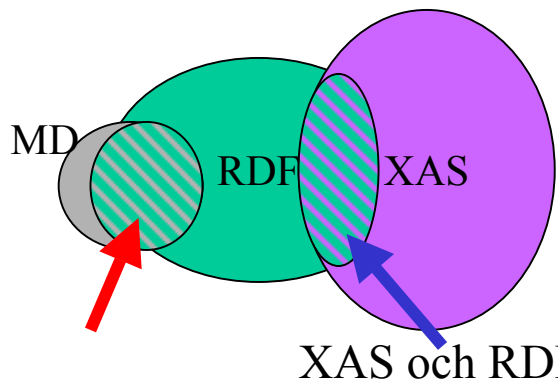


Both:
10% double donor
85% single donor
5% non donor

case a: elongation and bending case b: mainly elongation

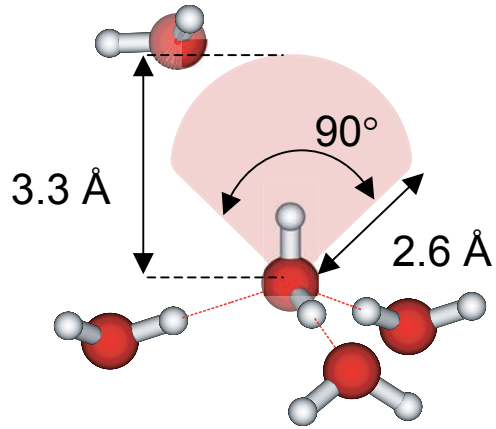


Wernet et. al. Science in press

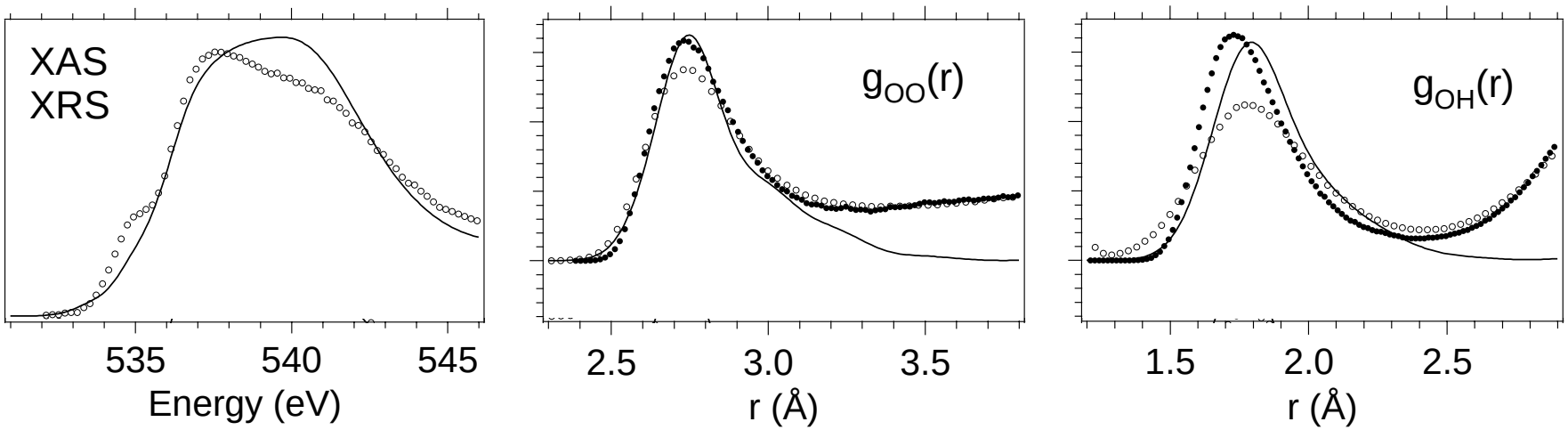


Analysis of MD simulations

In % at 25ºC	EXP	SPC/E	CPMD	MCYL
Double donor	10^{+15}_{-10}	70	76	50
Single donor	85 ± 15	27	23	41
Non donor	5 ± 5	3	1	9
No. of HB/molec.	***2.1 ± 0.4***	***3.3***	***3.5***	***2.8***

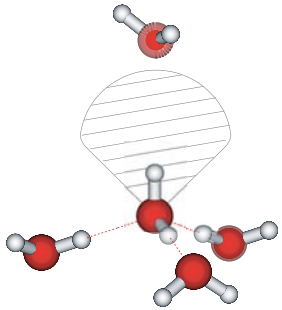


SPC/E



Too many straight intact H-bonds in SPC/E.

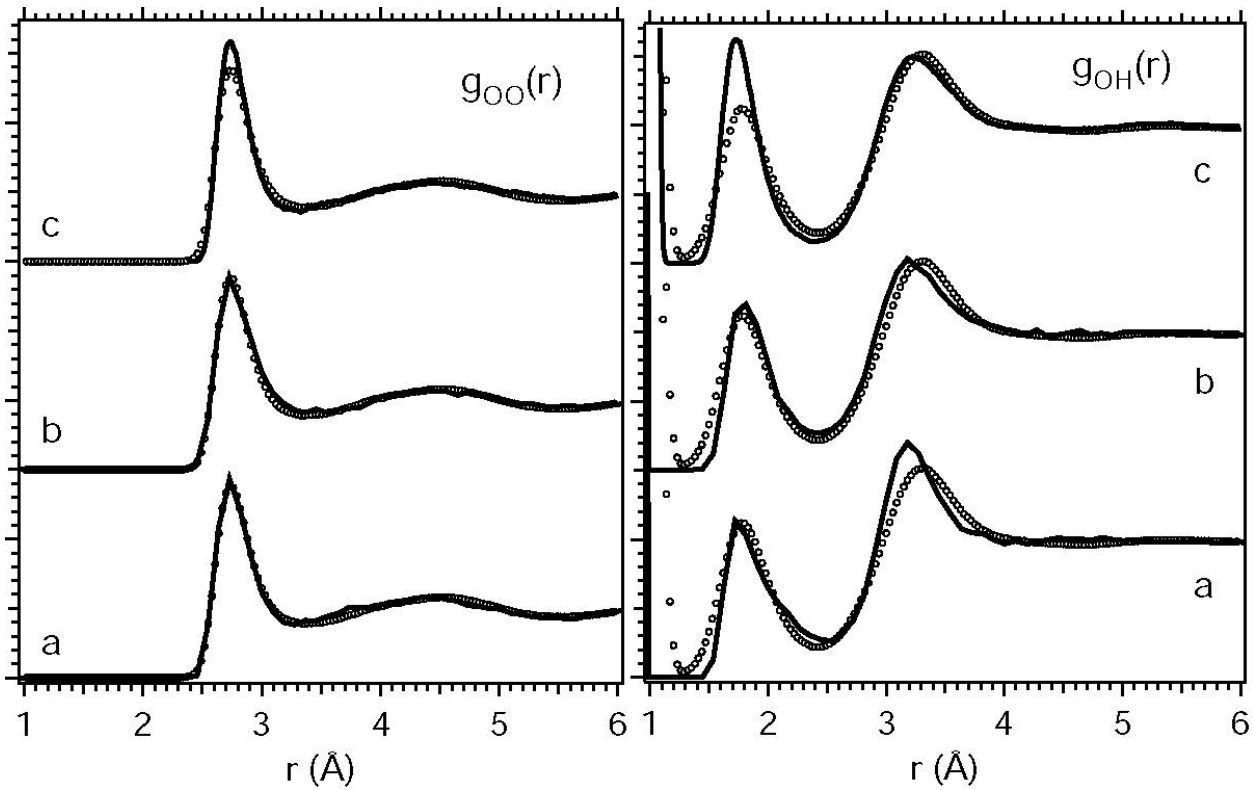
Extended Models



Case A: Artificial MD simulation by not allowing molecules to be in the cone, Results consistent with XAS

Case B: TIPP5 standard MD simulation

Case C: SPC MD simulation



Method	EXP+FIT	a	b	c
DD	10^{+15}_{-10}	25	75	70
SD	$85^{+}_{-}15$	75	23	27
ND	$5^{+}_{-}5$	0	2	3
TOTAL	100	100	100	100
n_{HB}	$2.1^{+}_{-}0.4$	2.5	3.5	3.3

Water on Ru(001)

a) Adsorbed at 150 K, scanning sample

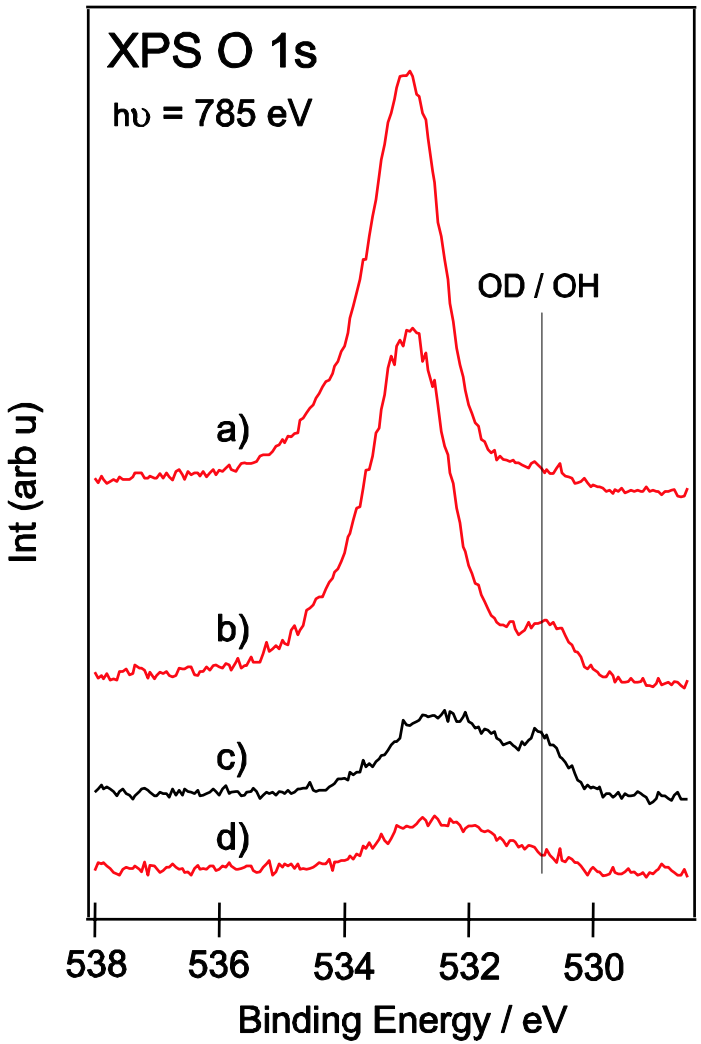
b) Radiation damage of a)

c) Exposure of H_2O at 180 K

d) Exposure of D_2O at 180 K

Non dissociative wetting

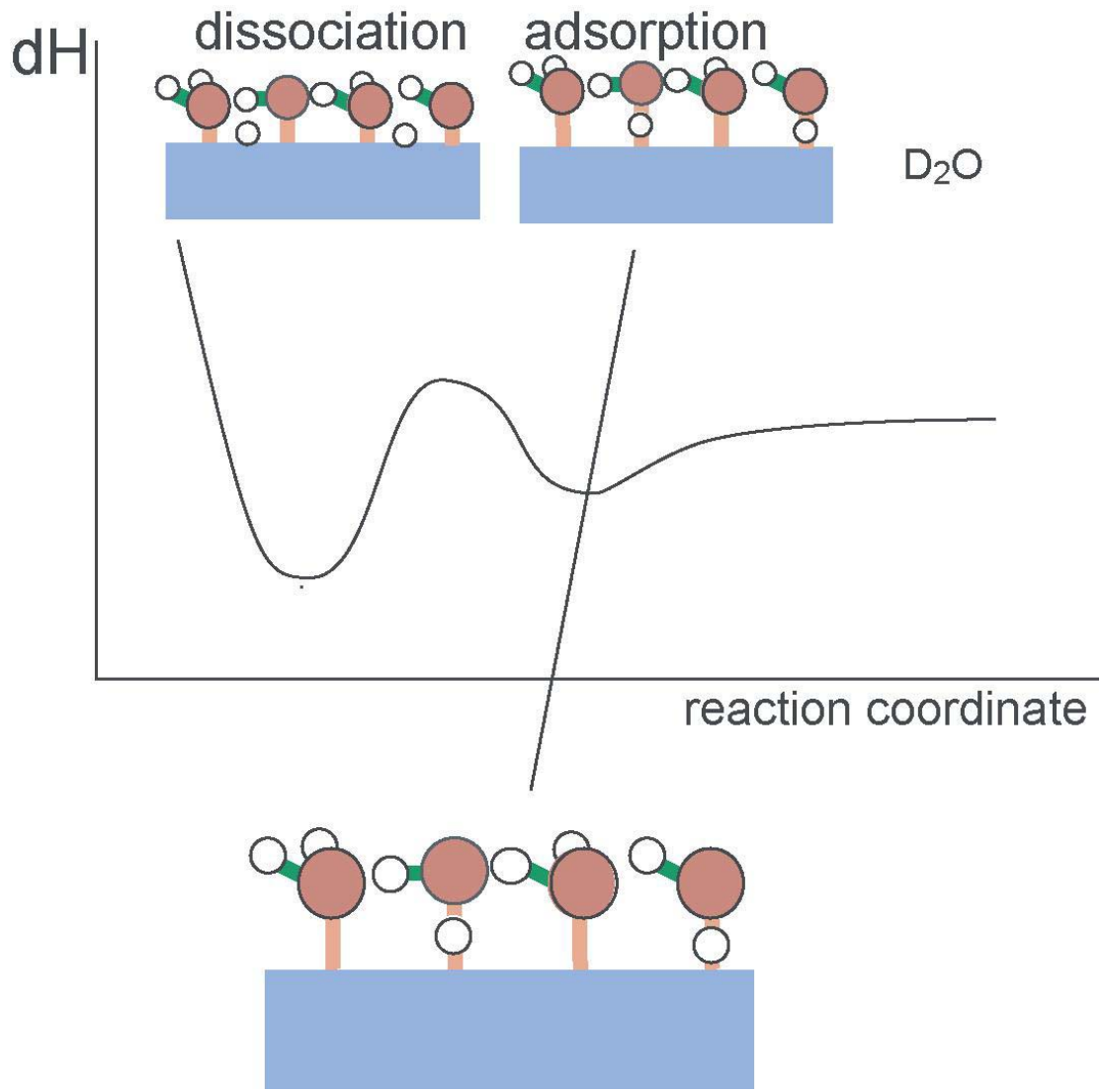
Activation barrier larger for Dissociation compared with Desorption



Water dissociation an activated process

Activation barrier larger for Dissociation compared with Desorption

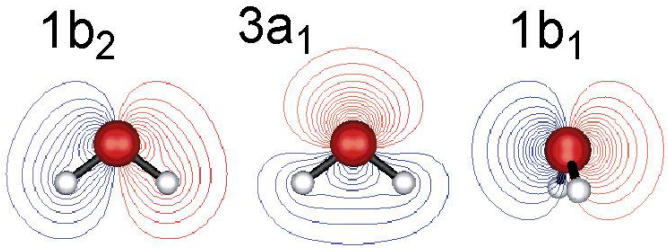
Question about dissociation; activation barrier more essential than total energy

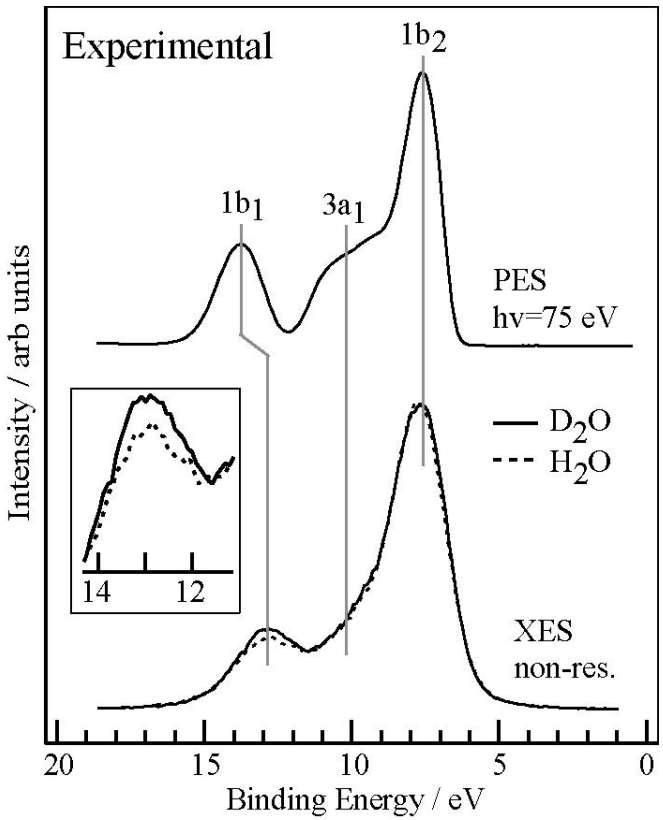


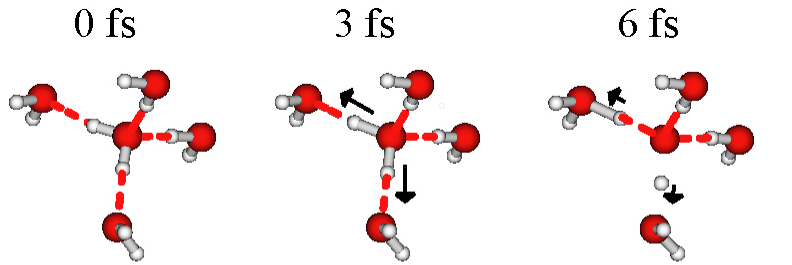
Outlook

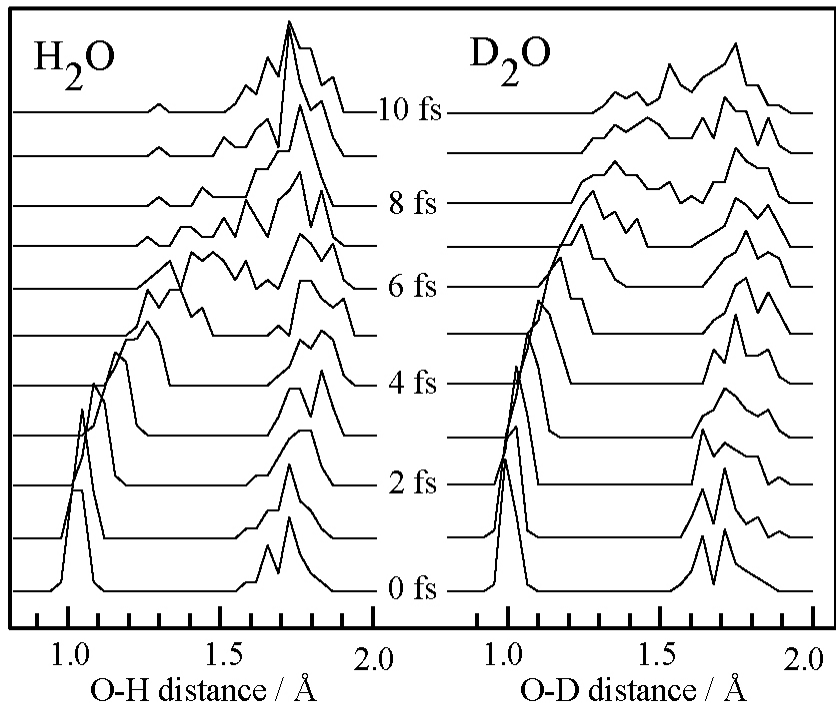
- X-ray spectroscopy can provide new unique information about hydrogen bonding structures in water and biological molecules
- Refinement of other structural techniques are essential to gain more detailed understanding, EXAFS and diffraction
- Improvement of MD simulations through comparison with experiments
- High and low density ice, supercooled water and supercritical water, the whole phase diagram
- Water in confinement, surfaces and interfaces
- Biological water, biomaterials
- Aqueous solutions
- Hydrophobic and hydrophilic water

Water dissociation





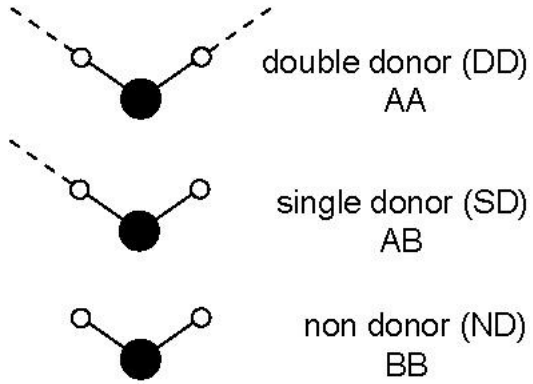




Broken H-bond configurations

Three main configurations:

Double donor:	both in
Single donor:	1 in, 1 out
Non donor:	both out



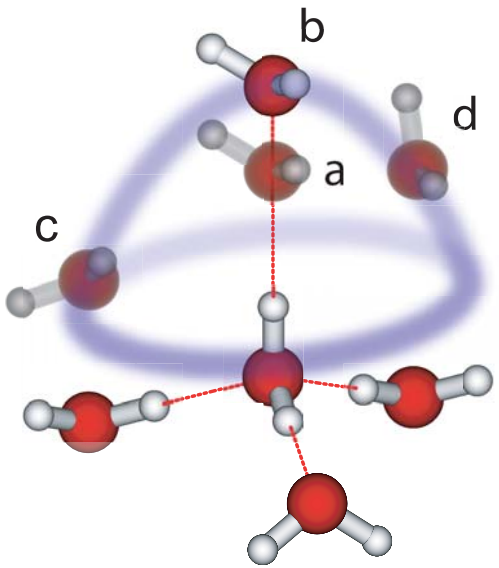
What do we mean by broken H-bonds in terms of geometry

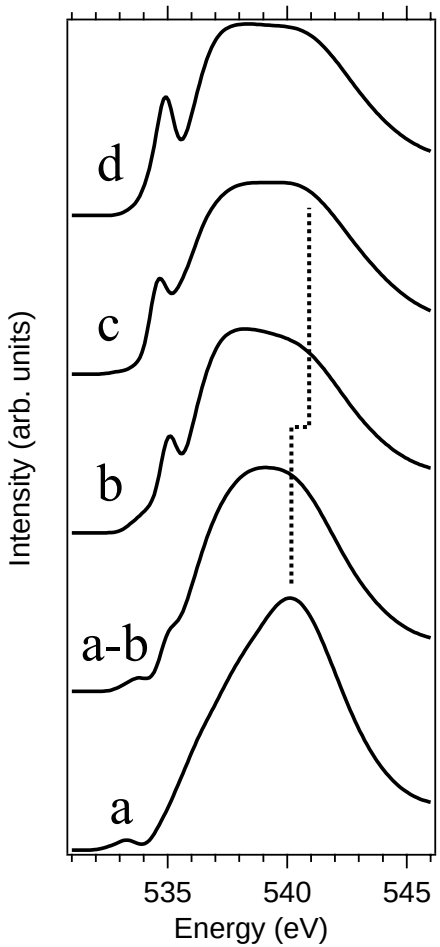
Bond length elongations and angular distortions

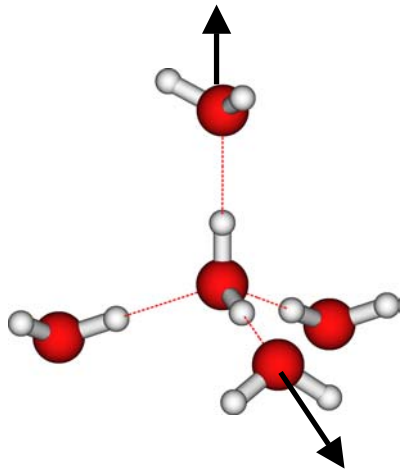
Breaking donor H-bonds

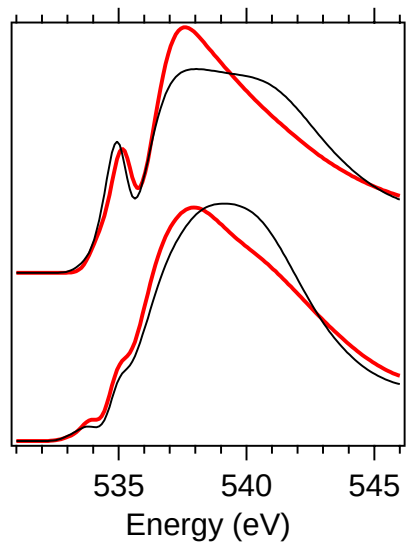
Move molecule on *one* H-side:

Move molecule on *both* H-sides:



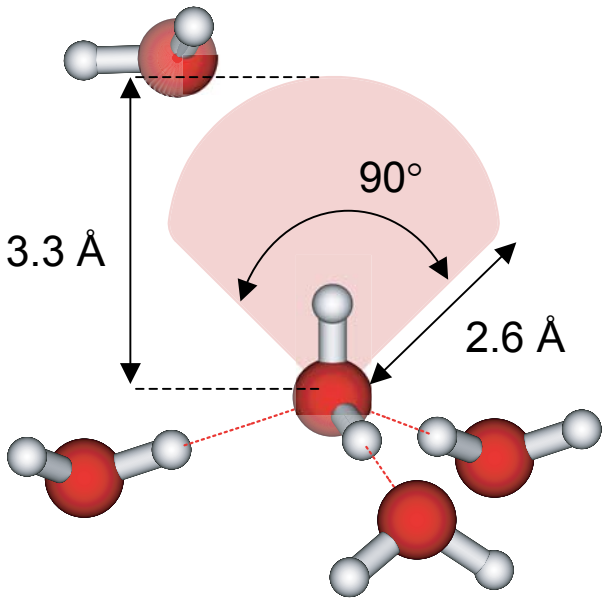




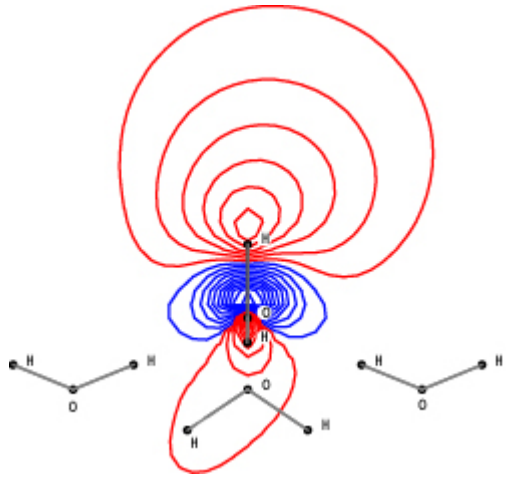


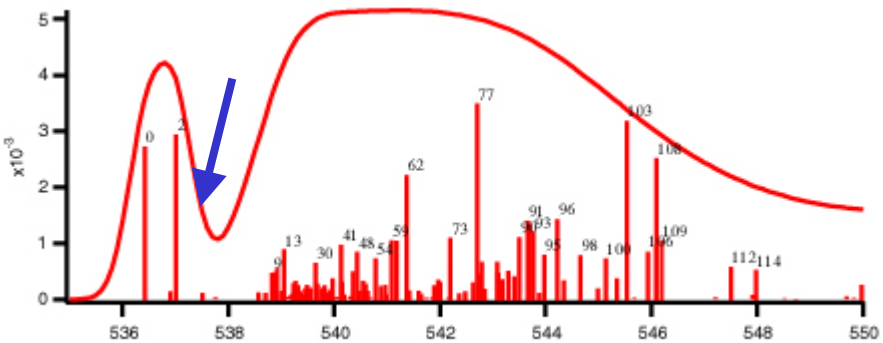
Wernet et. al. Science in press

Cone definition



Area where water molecule has to be excluded in order to generate the predge peak



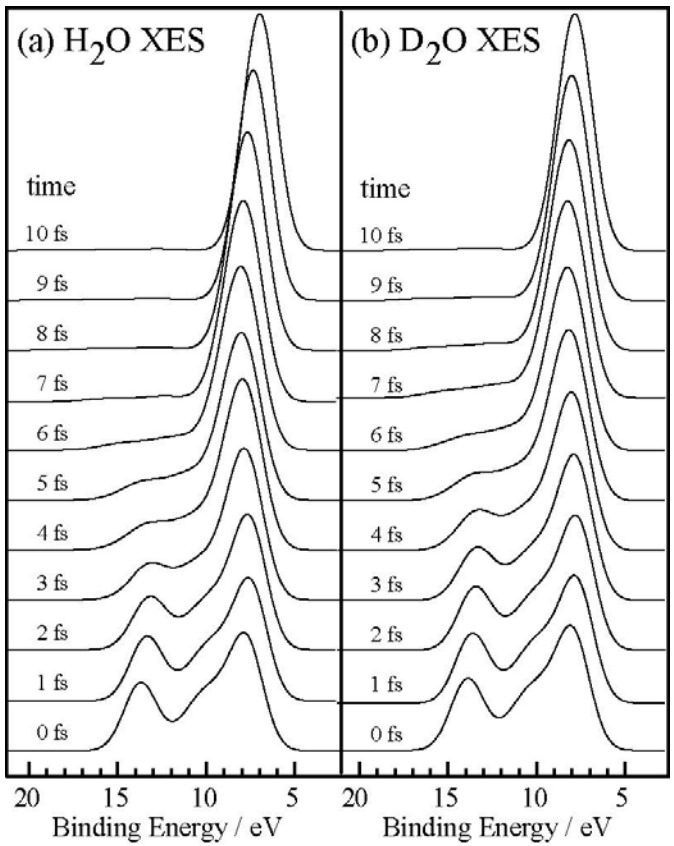


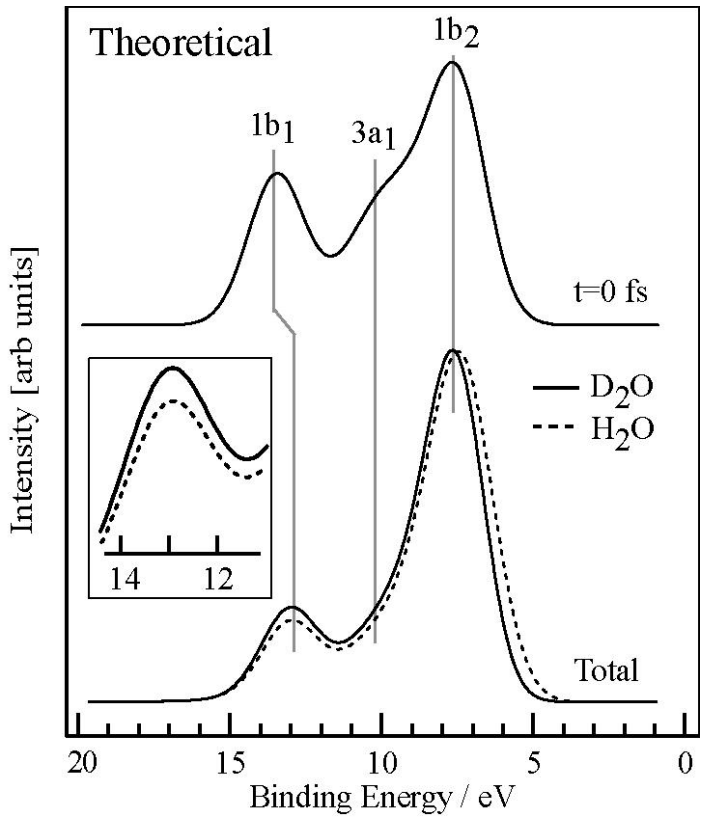
Wernet et. al. Science in press

Lowest excited states ($4a_1$ character) localize along free bond

Spatial extent similar to cone gives the sensitivity

Experimental spectra





O1s lifetime 3.6fs

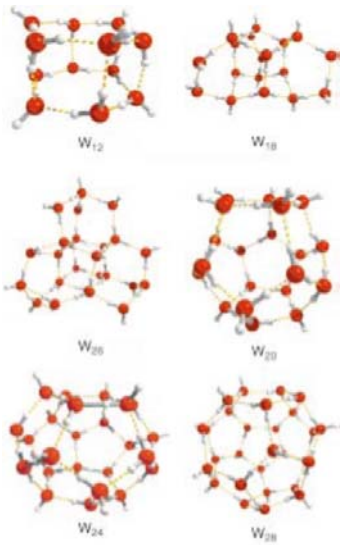
Cluster Equilibrium Theory

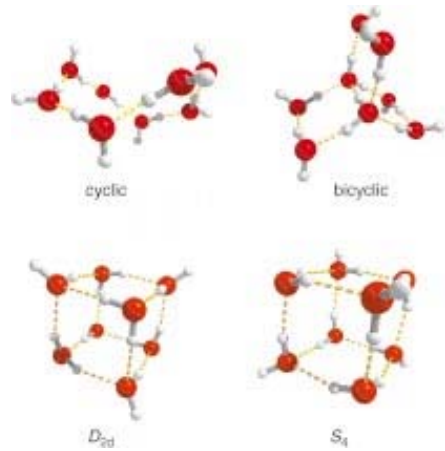
Weinhold et. al. J. Chem. Phys. 110, 508 (1999)

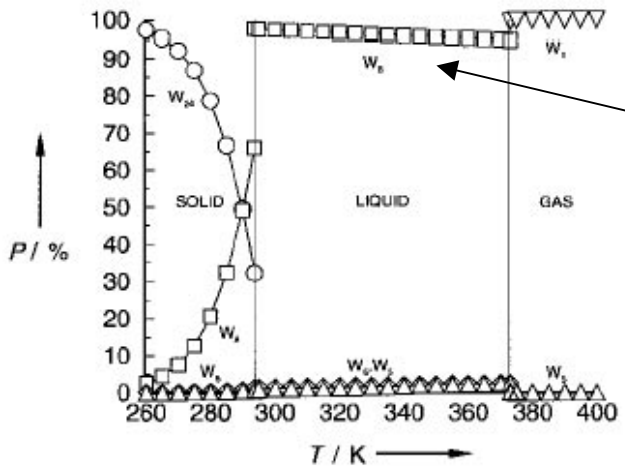
Renewal of old model

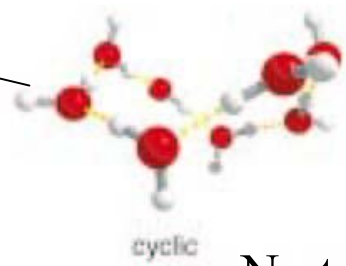
Thermodynamic equilibrium between different clusters

Properties of clusters obtained from quantum chemistry calculations









Cyclic Octamer dominates calculated distribution

All waters 2HB

No temperature dependence

Not consistent with MD simulations

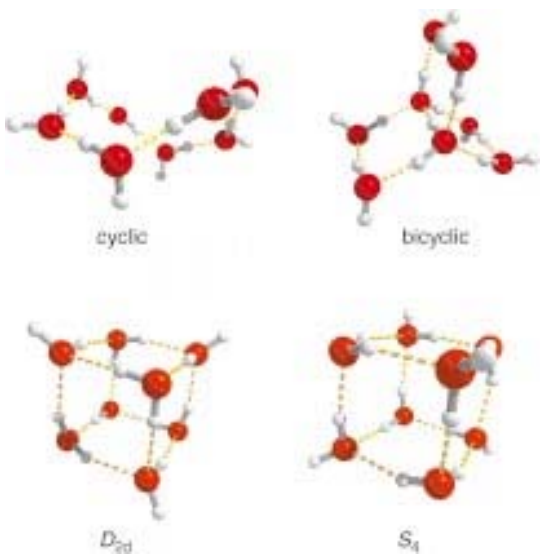
Stability of Clusters

Many Body Cooperativity effect

Hartree Fock Calculations by Wienhold

Large variation of H-bond strength

Cluster size	H-bond energy (kcal/mole)
2	6.0
5	10.7
8 (ring)	11.4
8 (cube)	7.6
20	7.7
26	9.0

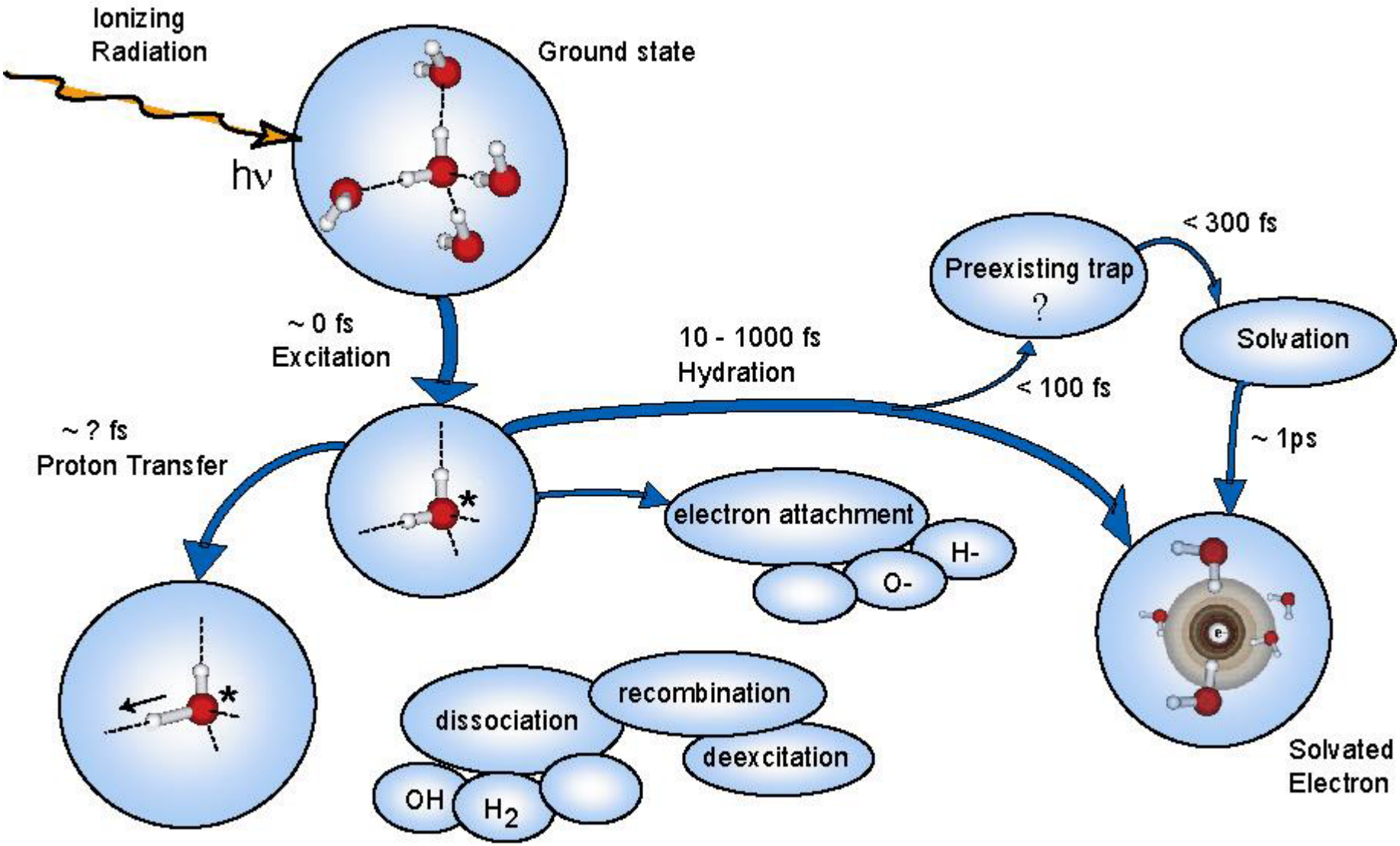


$$\Delta G = \Delta H - T\Delta S$$

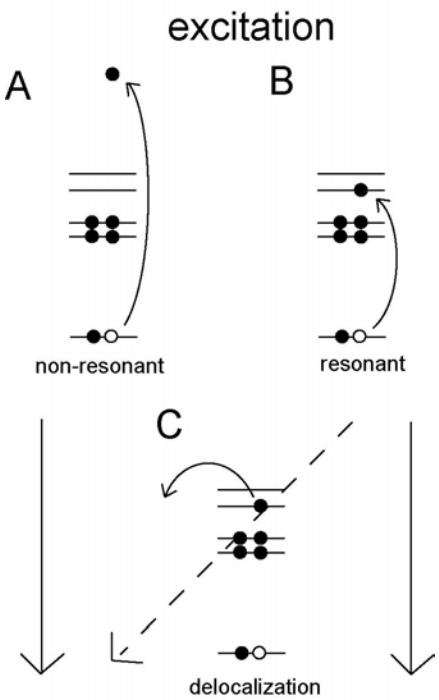
S: Entropi numbers of ways to partition the energy

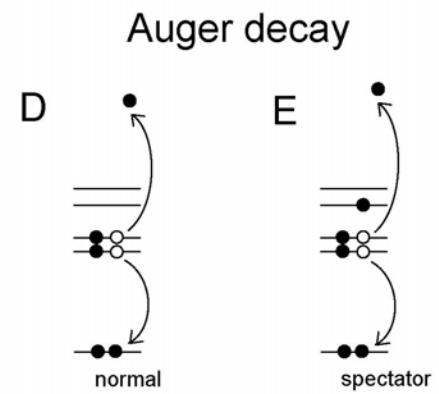
The cyclic octamer has more low energy modes of freedom compared with cubic octamer

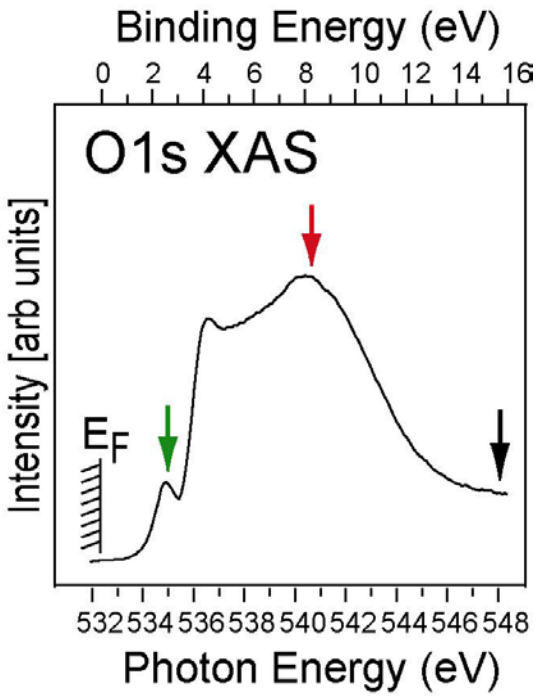
Ultrafast processes in ice

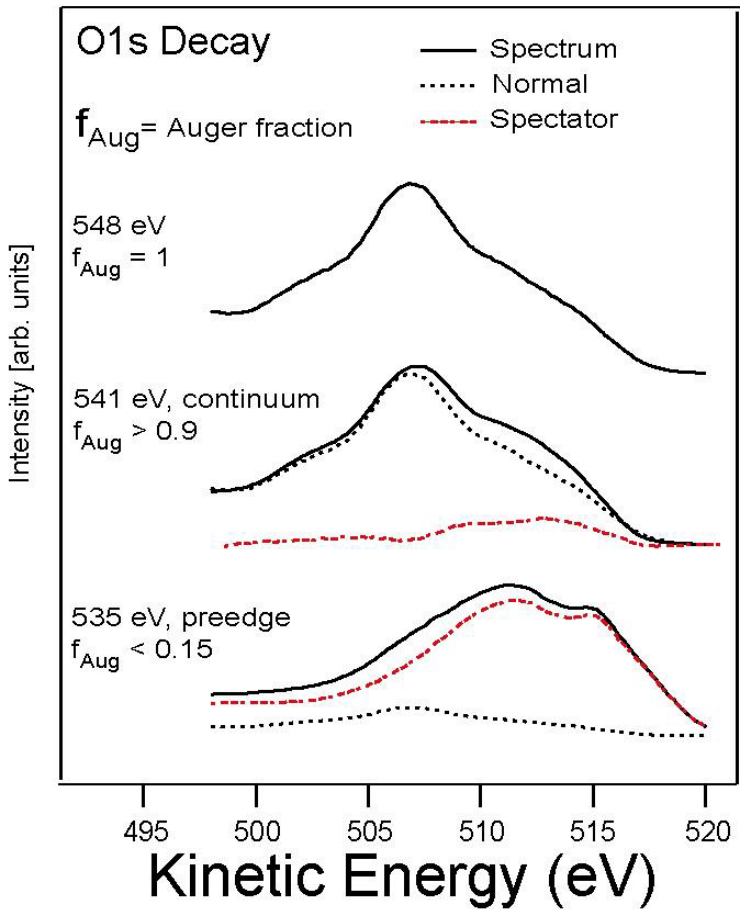


Electron delocalization in ice









Life time O1s 3.6 fs

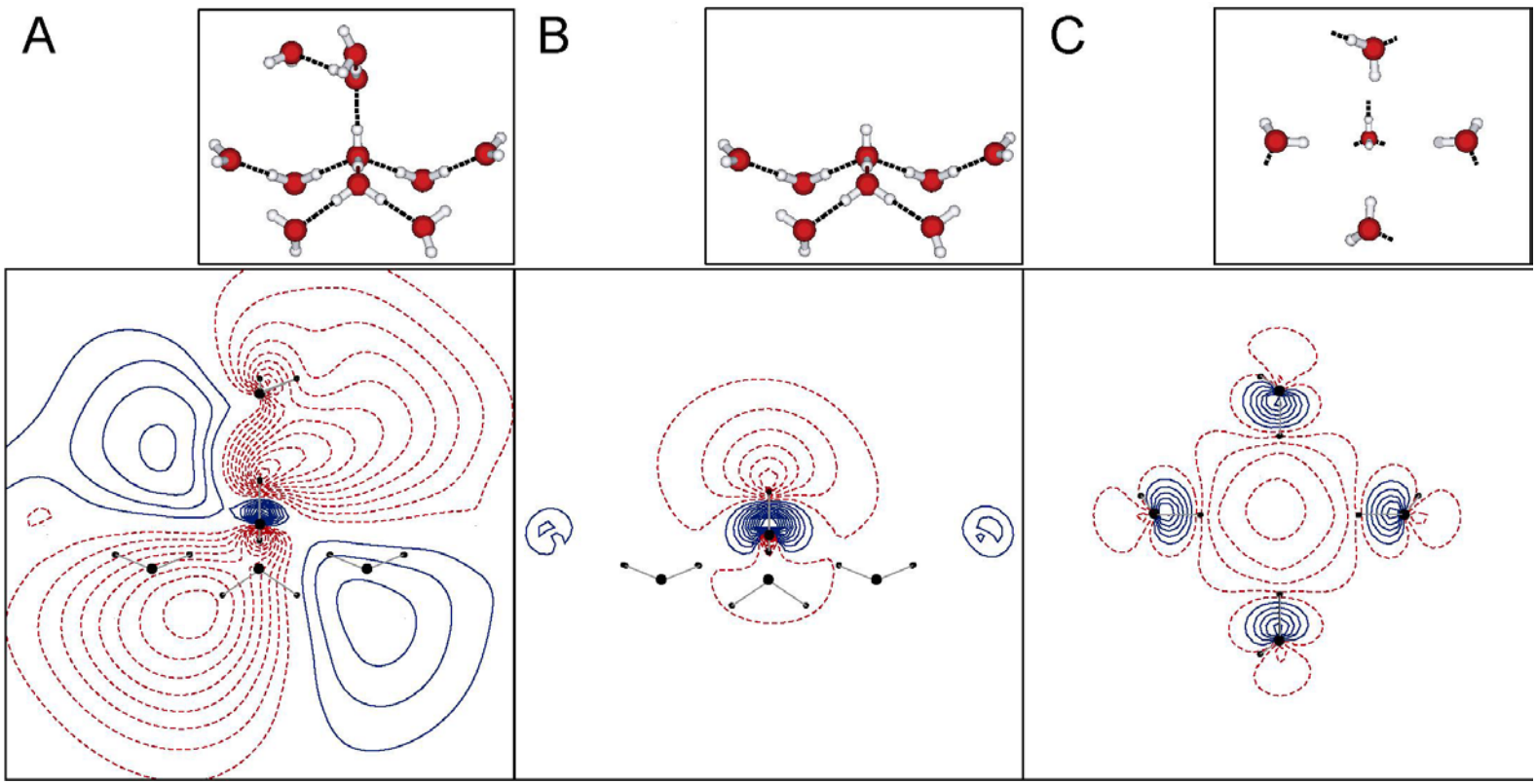
Predge ice surface slower than 20 fs

Conduction band bulk ice 0.5fs

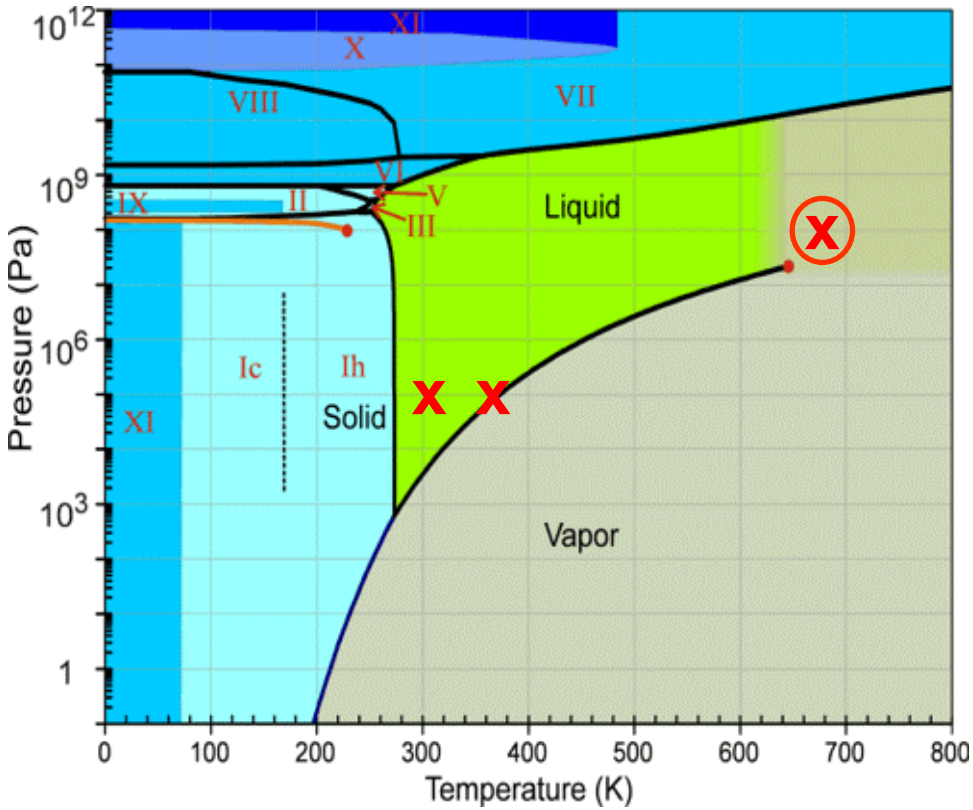
Solvated electrons

Orbital plots

Conduction band in ice | Broken H-bonds | Solvated electron



Supercritical water

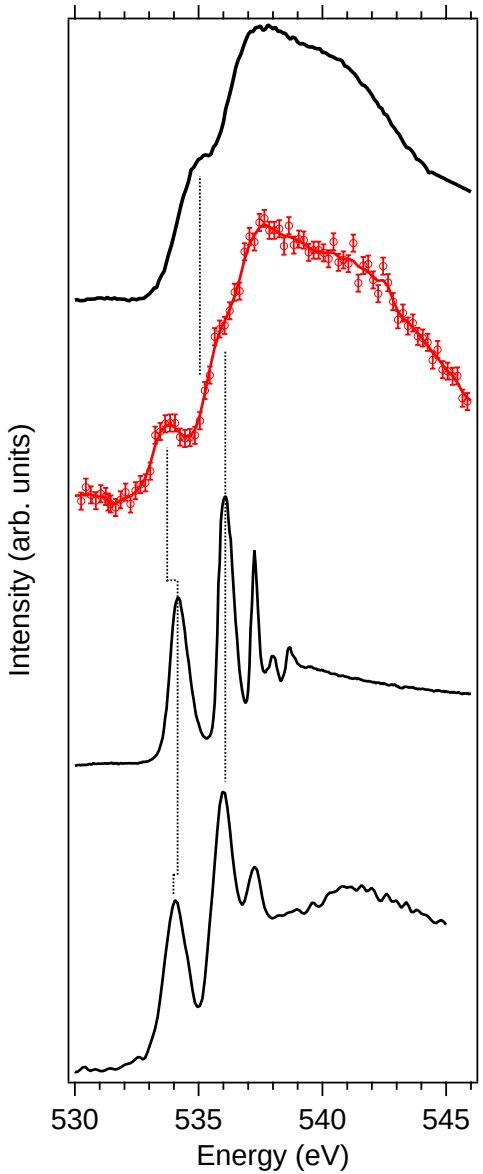


XRS

380 °C
300 bar
0.5 g/cm^3

- New phase
- Structure and bonding
- Properties of sc water
- Solvent for organics
- …

There are H-bonds in supercritical water



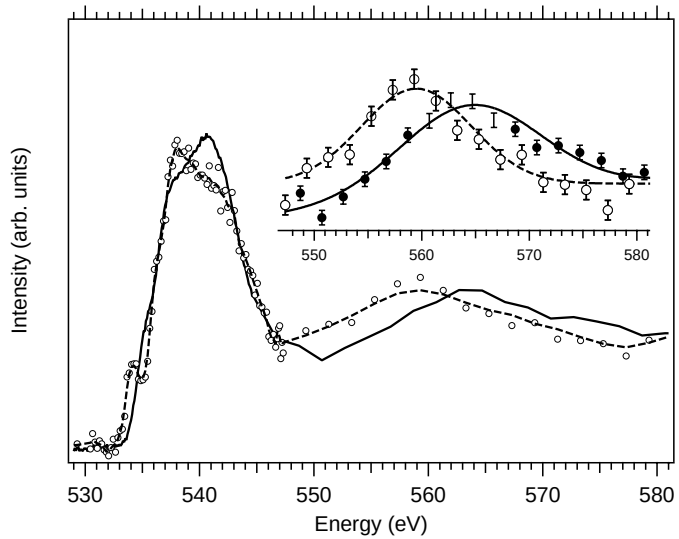
Ambient water

Sc water

Water vapor

Water surface (H^+ yield)

Wilson, Sakally et al., J. Phys.: Condens. Matter **14**, L221 (2002)



Shift of first EXAFS resonance

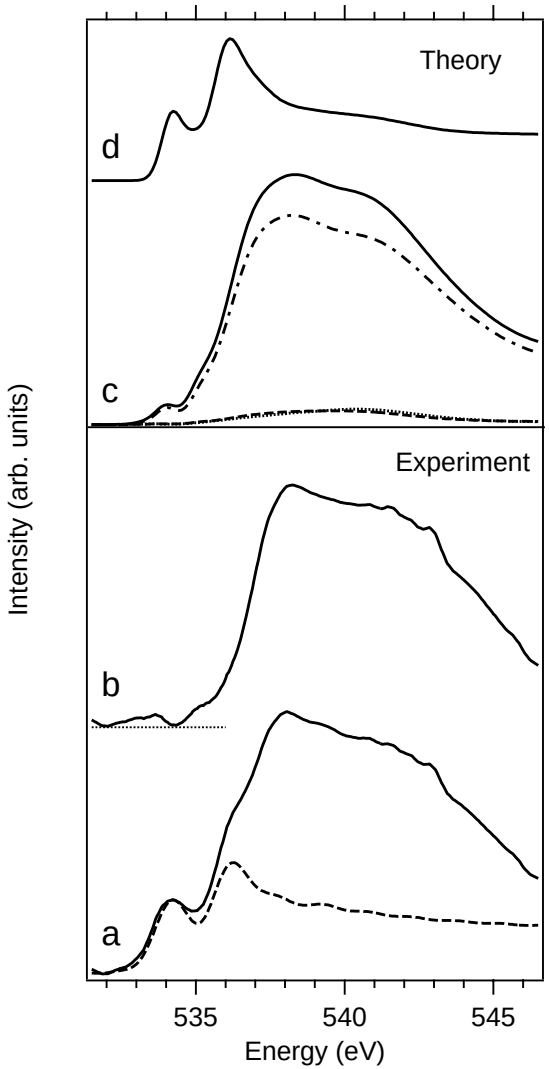
Bond length change of 0.4 Å

New peak @ ~534 eV
No peak @ ~535 eV
Strong @ 537-543 eV

~40% non donor species

~2.4 HB/molecule!

Model of Supercritical Water



Spectrum c calculated with tetrahedral coordination with 0.4 Å symmetrical elongation

MODEL

Region I: Hydrogen bonded Distorted tetrahedral coordination

Region II and III: Dominated by broken H-bonded species on both H-atoms